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(54) Title: METHOD AND COMPOSITION FOR MENTHOLATION OF CHARCOAL FILTERED CIGARETTES

(57) Abstract: The present invention relates to smoking articles such as cigarettes, and in particular to a method and composition for mentholation of smoking articles, including microencapsulation of menthol or other flavorants in a material melting below the pyrolysis zone of the smoking article.

METHOD AND COMPOSITION FOR MENTHOLATION OF CHARCOAL FILTERED CIGARETTES

Field of the Invention

The present invention relates to smoking articles such as cigarettes, and in particular to a method and composition for mentholation of smoking articles, including microencapsulation of menthol or other flavorants in a material melting below the pyrolysis zone of the smoking article.

Background of the Invention

Menthol, or 2-isopropyl-5-methyl-cyclohexanol, is a cyclic monoterpene. It is a major constituent of peppermint oil which has a minty taste and odor and which produces a cooling sensation when inhaled or consumed. Menthol is used as a flavorant in a variety of products, including toothpaste, mouthwashes, oral sprays, drugs, cough drops, cough lozenges, analgesic balms, inhalers, chewing gums, hard candies, chocolates, beverages, liquors, lotions, after-shave lotions, shampoo, moist towelettes, perfumes, deodorants, and the like.

Menthol is also a popular flavorant for use in cigarettes, pipe tobacco, chewing tobacco, and other smoking materials. It is used extensively because of the refreshing cooling effect it imparts to tobacco smoke. Menthol, however, has a high degree of volatility at room temperature. This volatility makes it difficult to control the concentration of menthol in cigarettes and can result in problems in packaging and handling. Smoking products containing menthol may also have a short shelf life due to loss of menthol from the product during storage. This problem is especially acute for menthol flavored cigarettes that also incorporate a charcoal filter. Menthol is irreversibly bound to charcoal and other adsorbants commonly used in filter cigarettes, and over time a substantial and unacceptable decrease in the available menthol results. Adsorption of menthol may also adversely affect the performance of the filter in removing undesirable components from the smoke generated during combustion of the tobacco product.

Accordingly, considerable time and expense has been spent on development of a satisfactory method for producing a menthol flavored charcoal filtered cigarette. Methods for mentholating unfiltered cigarettes or filtered cigarettes not incorporating an adsorbent are generally unsatisfactory for use on charcoal filtered cigarettes. For example, the classic

method of using mentholated strips sealed in a cigarette pack is unsatisfactory because the charcoal will simply absorb the menthol during storage, resulting in what is essentially a non-mentholated cigarette.

Other methods for producing mentholated smoking products that have been investigated have included providing menthol on a support, for example, diatomaceous earth, from which the menthol is later released. Such methods suffer from low menthol yields, and may result in unacceptable taste or appearance of the smoking product.

Other methods have focused on the preparation of menthol derivatives or similar compounds which release menthol or menthol-like flavorants upon pyrolysis or hydrolysis. Such derivatives include ester and carbonate derivatives of menthol, such as, for example, the derivatives disclosed in U.S. Pat. Nos. 3,312,226, 3,332,428, 3,419,543, 4,119,106, 4,092,988, 4,171,702, 4,177,339, and 4,212,310, 4,532,944, and 4,578,486. However, such derivatives may suffer from one or more drawbacks. For example, they may have a degree of volatility that makes them unsuited for use with adsorbents, they may not yield a sufficient quantity of free menthol upon decomposition, they may be unstable or difficult to process, or the pyrolysis or hydrolysis products may be toxic, carcinogenic, or may result in an unacceptable taste.

Summary of the Invention

While various methods have been provided for mentholating unfiltered cigarettes, no satisfactory method has been proposed for mentholating a cigarette or other smoking article incorporating a menthol adsorbing material, such as activated charcoal or zeolite. There is, therefore, a need for smoking materials containing an effective menthol delivery system that is compatible with the use of adsorbing filter materials.

In a first embodiment, a smoking composition is provided, the smoking composition including a smokable material, a plurality of microcapsules, and a filter, the smoking composition including a cigarette, wherein the smokable material includes a tobacco, the filter includes an activated charcoal or an activated carbon, and the microcapsules include a shell material and a filler material, wherein the filler material includes menthol, and wherein the shell material includes a waxy thermomeltable material having a melting point of from about 35°C to about 200°C.

In a second embodiment, a smoking composition is provided including a smokable material and a plurality of microcapsules, the microcapsules including a shell material and a

filler material, wherein the shell material melts upon exposure to a temperature above an ambient temperature and below a pyrolysis temperature of the smokable material, whereby the filler material is released into a mainstream smoke, a sidestream smoke, or both the mainstream smoke and the sidestream smoke.

In an aspect of the second embodiment, the smokable material includes tobacco. The tobacco may have a reduced or a negligible nicotine content, or a reduced or a negligible content of a tobacco-specific nitrosamine.

In an aspect of the second embodiment, the filler material includes a flavorant, such as menthol.

In an aspect of the second embodiment, the smoking composition further includes a filter. The filter may further include an activated charcoal or an activated carbon. The filter may include a cavity filter. The cavity filter may be at least 95 vol. % filled, or about 100 vol. % filled.

In an aspect of the second embodiment, the shell material includes a waxy thermomelttable material having a melting point of from about 35°C to about 200°C. The waxy thermomelttable material may include carnauba wax, montan wax, ouricury wax, candelilla wax, coconut wax, paraffin wax, beeswax, spermaceti wax, microcrystalline wax, rice wax, low molecular weight polyethylene wax, stearic acid, palmitic acid, myristic acid, stearylamine, stearone, or mixtures thereof.

In an aspect of the second embodiment, the shell material includes a water insoluble polymer. The water insoluble polymer may include cellulose ethers, cellulose esters, ureaformaldehyde resins, polyvinyl chloride, polyvinylidene chloride, polyethylene, polypropylene, polyacrylates, polymethacrylates, polymethyl-methacrylates, nylon, or mixtures thereof.

In an aspect of the second embodiment, the shell material includes a water soluble polymer. The water soluble polymer may include polyvinyl pyrrolidone, water soluble celluloses, polyvinyl alcohol, ethylene maleic anhydride copolymer, and methyl vinyl ether maleic anhydride copolymer, polyethylene oxides, water soluble polyamide, water soluble polyesters, polymers of acrylic acid, polystyrene acrylic acid copolymers, or mixtures thereof.

In an aspect of the second embodiment, the shell material includes starch, gums, gelatin, dextrans, hydrolyzed gums, hydrolyzed gelatin, gum arabic, larch, pectin,

tragacanth, locust bean, guar, alginates, carrageenans, carboxy methyl cellulose, karaya, maltodextrins, or mixtures thereof.

In a third embodiment, a method for providing a smokable material including a volatile flavorant is provided, the method including providing a plurality of microcapsules including a shell material and a filler material, the filler material including a volatile flavorant, wherein the shell material melts upon exposure to a temperature above an ambient temperature and below a pyrolysis temperature of the smokable material; and depositing the microcapsules on the smokable material, whereby a smokable material including a volatile flavorant is obtained.

In an aspect of the third embodiment, the smokable material includes tobacco.

In an aspect of the third embodiment, the volatile flavorant includes menthol.

In an aspect of the third embodiment, the shell material includes a waxy thermomelttable material having a melting point of from about 35°C to about 200°C.

Detailed Description of the Preferred Embodiments

Introduction

The following description and examples further illustrate the preferred embodiments of the present invention. Those of skill in the art will recognize that there are numerous variations and modifications of this invention that are encompassed by its scope. Accordingly, the description of preferred embodiments should not be deemed to limit the scope of the present invention.

In preferred embodiments, methods and compositions for delivering menthol or other flavorants into the smoke stream of a smoking article, such as a cigarette, are provided. The method involves microencapsulation of the flavorant and incorporation of the microcapsules into the smoking article. The microcapsules isolate the flavorant from adsorbents, such as activated charcoal, and provide for the controlled release of the flavorant during smoking, as well as provide for a longer shelf life for the smokable article than is possible when unencapsulated flavorants are present. The shell wall of the microcapsule is preferably sufficiently compatible with the flavorant contained therein to retain the flavorant until such time as the heat generated during smoking causes the shell to open. Encapsulating materials that melt rather than volatilize are generally preferred so as to prevent introduction of the shell material into the smoke stream.

The preferred embodiments relate to smoking articles such as cigarettes, cigars, or pipe tobacco, and in particular to cigarettes having reduced content of various polyaromatic hydrocarbons (PAHs), tobacco specific nitrosamines (TSNAs), phenolic compounds, and certain other undesired components in cigarette smoke, including both mainstream and sidestream smoke, or having reduced content of nicotine or other undesired components in the uncombusted smoking product. The tobacco products of preferred smoking articles may also include a catalytic system including metallic or carbonaceous particles and a source of nitrate or nitrite, as described in copending United States Application Ser. No. 10/007,724 filed on November 9, 2001, the disclosure of which is incorporated herein by reference in its entirety. The preferred smoking articles for use with the microcapsules of preferred embodiments typically incorporate an activated charcoal filter. However the microcapsules are also suitable for use with unfiltered smoking articles.

While the compositions and methods of preferred embodiments generally refer to tobacco, particularly in the form of cigarettes, it is to be understood that such compositions and methods encompass any smokable material or smokable composition, as will be apparent to one skilled in the art. Likewise, while the compositions and methods of preferred embodiments generally refer to menthol, it is to be understood that such compositions and methods encompass any flavorant, volatile material adsorbable by activated charcoal, or any other additive wherein it may be desirable to encapsulate the additive for release upon exposure to heat generated by combustion or pyrolysis of the smokable material.

Flavorants

Any suitable flavorant, odorant, additive, or other volatile component that is capable of being adsorbed by activated charcoal or any other adsorbent which may be present in a smoking article may be added to a smoking material in the form of microcapsules. Preferred flavorants include, but are not limited to, menthol, menthol derivatives, menthol precursors, and other compounds capable of imparting menthol-like flavoring.

Suitable flavorants include natural fragrances, synthetic fragrances, synthetic essential oils, and natural essential oils. Examples of synthetic fragrances include, but are not limited to, terpenic hydrocarbons, esters, ethers, alcohols, aldehydes, phenols, ketones, acetals, oximes, and mixtures thereof. Examples of terpenic hydrocarbons include, but are not limited to, lime terpene, lemon terpene and limonene dimer. Examples of essential oils

include, but are not limited to, natural oils obtained from *Angelica archangelica*, *Pimpinella anisum*, *Myroxylon pereirae*, *Ocimum basilicum*, *Pimenta racemosa*, *Laurus Nobilis*, *Apis mellifera*, *Styrax tonkinensis*, *Citrus bergamia*, *Mentha citrata*, *Aniba roseodora*, *Boronia megastigma*, *Melaleuca leucadendron*, *Elettaria cardamomum*, *Daucus carota*, *Cedrus atlantica*, *Juniperus virginiana*, *Matricaria chamomilla*, *Anthemis nobilis*, *Cinnamomum zeylanicum*, *Cymbopogon nardus*, *Salvia sclarea*, *Eugenia caryophyllata*, *Coriandrum sativum*, *Cupressus sempervirens*, *Anethum graveolens*, *Canarium luzonicum*, *Eucalyptus globulus*, *Eucalyptus citriodora*, *Eucalyptus radiata*, *Foeniculum vulgare*, *Abies alba*, *Boswellia carterii*, *Ferula galbaniflua*, *Pelargonium graveolens*, *Pelargonium roseum*, *Zingiber officinale*, *Citrus paradisi*, *Helichrysum angustifolia*, *Hyssopus officinalis*, *Helichrysum angustifolia*, *Jasminum officinalis*, *Juniperus communis*, *Leptospermum ericoides*, *Lavandula officinalis*, *Lavandula hybrida*, *Citrus limon*, *Cymbopogon citratus*, *Citrus aurantifolia*, *Tilia vulgaris*, *Citrus reticulata*, *Leptospermum scoparium*, *Origanum majorana*, *Litsea cubeba*, *Commiphora myrrha*, *Myrtus communis*, *Backhousia citriodora*, *Citrus aurantium*, *Melaleuca quinquenervia*, *Myristica fragrans*, *Evernia prunastri*, *Boswellia carterii*, *Citrus aurantium*, *Citrus sinensis*, *Oreganum vulgare*, *Cymbopogon martini*, *Petroselinum sativum*, *Pogostemon cablin*, *Piper nigrum*, *Mentha piperita*, *Citrus aurantium*, *Pinus sylvestris*, *Ravensara aromatica*, *Rosa damascena*, *Rosmarinus officinalis*, *Aniba roseodora*, *Santalum album*, *Mentha spicata*, *Nardostachys jatamansi*, *Picea mariana*, *Tagetes minuta*, *Citrus reticulata*, *Melaleuca alternifolia*, *Leptospermum petersonii*, *Leptospermum scoparium*, *Thymus vulgaris*, *Nicotiana tabacum*, *Polianthes tuberosa*, *Vanilla planifolia*, *Vetiveria zizanioides*, *Viola odorata*, *Achillea millefolium*, *Cananga odorata*, *Trachyspermum copticum*, *Prunus dulcis* var. *amara*, *Arnica Montana*, *Betula lenta*, *Peumus boldus*, *Spartium junceum*, *Acorus calamus* var. *angustatus*, *Cinnamomum camphora*, *Carphephorus odoratissimus*, *Allium sativum*, *Armoracia rusticana*, *Pilocarpus jaborandi*, *Melilotus officinalis*, *Artemisia vulgaris*, *Brassica nigra*, *Allium cepa*, *Mentha pulegium*, *Ruta graveolens*, *Sassafras albidum*, *Thuja occidentalis*, *Gaultheria procumbens*, *Chenopodium ambrosioides* var. *anthelminticum*, and *Artemisia absinthium*, and the synthetic versions thereof.

Other suitable flavors include include various aromatic aldehydes, ketones, and alcohols. Examples of aldehyde flavors include acetaldehyde (apple), benzaldehyde (cherry, almond), anisic aldehyde (licorice, anise), cinnamic aldehyde (cinnamon), citral or alpha

citral (lemon, lime), neral or beta citral (lemon, lime), decanal (orange, lemon), ethyl vanillin (vanilla, cream), heliotropine or piperonal (vanilla, cream), vanillin (vanilla, cream), alpha-amyl cinnamaldehyde (spicy fruity flavors), butyraldehyde (butter, cheese), valeraldehyde (butter, cheese), citronellal, decenal (citrus fruits), aldehyde C-8 (citrus fruits), aldehyde C-9 (citrus fruits), aldehyde C-12 (citrus fruits), 2-ethyl butyraldehyde (berry fruits), hexenal (berry fruits), tolyl aldehyde (cherry, almond), veratraldehyde (vanilla), 2-6-dimethyl-5-heptenal (melon), 2,6-dimethyloctanal (green fruit), and 2-dodecenal (citrus, mandarin). Examples of ketone flavors include d-carvone (caraway), 1-carvone (spearmint), diacetyl (butter, cheese, cream), benzophenone (fruity and spicy flavors, vanilla), methyl ethyl ketone (berry fruits), maltol (berry fruits), menthone (mints), methyl amyl ketone, ethyl butyl ketone, dipropyl ketone, methyl hexyl ketone, ethyl amyl ketone (berry fruits, stone fruits), pyruvic acid (smokey, nutty flavors), acetanisole (hawthorn heliotrope), dihydrocarvone (spearmint), 2,4-dimethylacetophenone (peppermint), 1,3-diphenyl-2-propanone (almond), acetocumene (orris and basil, spicy), isojasnone (jasmine), d-isomethylionone (orris-like, violet), isobutyl acetoacetate (brandy-like), zingerone (ginger), pulegone (peppermint-camphor), d-piperitone (minty), and 2-nonanone (rose and tea-like). Examples of alcohol flavors include anisic alcohol or p-methoxybenzyl alcohol (fruity, peach), benzyl alcohol (fruity), carvacrol or 2-p-cymenol (pungent warm odor), carveol, cinnamyl alcohol (floral odor), citronellol (rose odor), decanol, dihydrocarveol (spicy, peppery), tetrahydrogeraniol or 3,7-dimethyl-1-octanol (rose odor), eugenol (clove), and perillyl alcohol (floral-pine).

Other suitable flavorants include aromatic esters including, but not limited to, γ -undecalactone, ethyl methyl phenyl glycidate, allyl caproate, amyl salicylate, amyl benzoate, amyl acetate, benzyl acetate, benzyl benzoate, benzyl salicylate, benzyl propionate, butyl acetate, benzyl butyrate, benzyl phenylacetate, cedryl acetate, citronellyl acetate, citronellyl formate, p-cresyl acetate, 2-t-pentyl-cyclohexyl acetate, cyclohexyl acetate, cis-3-hexenyl acetate, cis-3-hexenyl salicylate, dimethylbenzyl acetate, diethyl phthalate, δ -deca-lactone dibutyl phthalate, ethyl butyrate, ethyl acetate, ethyl benzoate, fenchyl acetate, geranyl acetate, γ -dodecalatone, methyl dihydrojasmonate, isobornyl acetate, β -isopropoxyethyl salicylate, linalyl acetate, methyl benzoate, o-t-butylcyclohexyl acetate, methyl salicylate, ethylene brassylate, ethylene dodecanoate, methyl phenyl acetate, phenylethyl isobutyrate, phenylethylphenyl acetate, phenylethyl acetate, methyl phenyl

carbinyl acetate, 3,5,5-trimethylhexyl acetate, terpinyl acetate, triethyl citrate, p-t-butylcyclohexyl acetate and vetiver acetate.

Also suitable are aromatic ethers including, but not limited to, p-cresyl methyl ether, diphenyl ether, 1,3,4,6,7,8-hexahydro-4,6,7,8,8-hexamethyl cyclopenta- β -2-benzopyran and phenyl isoamyl ether.

Other substances that may be incorporated into the microcapsules of preferred embodiments include various excipients and other substances well known in the art of smoking article formulations or microcapsule formulations. Such substances are preferably nontoxic and do not yield undesirable decomposition products or impart an unpleasant taste when the smoking material is combusted. These other substances may include ionic and nonionic surfactants (e.g., PLURONIC™, TRITON™), detergents (e.g., polyoxyl stearate, sodium lauryl sulfate), emulsifiers, demulsifiers, stabilizers, aqueous and oleaginous carriers (e.g., white petrolatum, isopropyl myristate, lanolin, lanolin alcohols, mineral oil, sorbitan monooleate, propylene glycol, cetylstearyl alcohol), solvents, preservatives (e.g., methylparaben, propylparaben, benzyl alcohol, ethylene diamine tetraacetate salts), thickeners (e.g., pullulin, xanthan, polyvinylpyrrolidone, carboxymethylcellulose), plasticizers (e.g., glycerol, polyethylene glycol), antioxidants (e.g., vitamin E), buffering agents, and the like.

Microencapsulated Flavorants

Certain flavorants may have a high degree of volatility. This volatility may result in loss of the flavorant through adsorption by filter materials or escape through packaging during storage. Microencapsulation is an effective technique to avoid undesired loss of flavorant prior to use of the smoking article.

In a preferred embodiment, menthol is entrapped into hydrophilic gelatin microcapsules and mixed with cut tobacco. Other preferred shell materials include water soluble alcohols and polyethylene oxides. The microcapsule's shell blocks loss of the flavorant by volatilization. Microencapsulation permits volatile flavorants to be used with adsorbing filter materials in smoking products. The microencapsulated flavorants provide controlled release of the flavorant from the microcapsule at a preselected temperature, typically from slightly below the pyrolysis temperature of the smoking material down to slightly above room temperature. However, higher temperatures may be preferred for certain applications.

Microencapsulation techniques involve the coating of small solid particles, liquid droplets, or gas bubbles with a thin film of a material, the material providing a protective shell for the contents of the microcapsule. Microcapsules suitable for use in the preferred embodiments may be of any suitable size, typically from about 1 μm or less to about 1000 μm or more, preferably from about 2 μm to about 50, 60, 70, 80, 90, 100, 200, 300, 400, 500, 600, 700, 800, or 900 μm , and more preferably from about 3, 4, 5, 6, 7, 8, or 9 μm to about 10, 15, 20, 25, 30, 35, 40 or 45 μm . In certain embodiments, it may be preferred to use nanometer-sized microcapsules. Such microcapsules may range from about 10 nm or less up to less than about 1000 nm (1 μm), preferably from about 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, or 90 nm up to about 100, 200, 300, 400, 500, 600, 700, 800, or 900 nm.

While in many embodiments a solid phase flavorant or other substance, such as menthol, is encapsulated, in certain embodiments it may be preferred to encapsulate a liquid or gaseous substance. Liquid or gas containing microcapsules may be prepared using conventional methods well known in the art of microcapsule formation, and such microcapsules may be incorporated into the smoking articles of the preferred embodiments.

Microcapsule Components

The microcapsules of preferred embodiments contain a filling material. The filling material is typically one or more flavorants, optionally in combination with substances other than flavorants. In certain embodiments, it may be preferred that the microcapsules contain one or more substances not including flavorants. The filling material is encapsulated within the microcapsule by a shell material.

Typical shell materials may include, but are not limited to, gum arabic, gelatin, ethylcellulose, polyurea, polyamide, aminoplasts, maltodextrins, and hydrogenated vegetable oil. While any suitable shell material may be used in the preferred embodiments, it is generally preferred to use an edible or nontoxic shell material approved for use in food or pharmaceutical applications. It is also preferred to use a shell material that melts at a temperature below the pyrolysis temperature of the smokable material. Temperatures in the combustion zone of tobacco are typically from about 600°C to about 900°C, and those in the pyrolysis/distillation zone are typically between about 200°C and 600°C. The most preferred shell materials are those that melt at a temperature below about 200°C, but above the highest ambient temperature that the cigarette may be exposed to prior to use. Such

shell materials may include waxes, polymers, fats, hydrogenated vegetable oils, and other substances with suitable melting points.

In certain preferred embodiments, the encapsulating material is a waxy thermomelttable material having a melting point of from about 35°C or lower to about 200°C or higher, more preferably from about 36°C, 37°C, 38°C, 39°C, or 40°C to about 150°C, 160°C, 170°C, 180°C, or 190°C, and most preferably from about 41°C, 42°C, 43°C, 44°C, 45°C, 50°C, 60°C, 70°C, 80°C, 90°C or 100°C to about 110°C, 120°C, 130°C, or 140°C. Examples of suitable materials include, but are not limited to, carnauba wax, montan wax, ouricury wax, candelilla wax, coconut wax, paraffin wax, microcrystalline wax, Hoechst wax (such as OP and O), Bareco wax (such as WB wax), NPS wax, rice wax, low molecular weight polyethylene wax, stearic acid, palmitic acid, myristic acid, fatty acid amide (such as stearylamine) and ketone wax (such as stearone). Any suitable waxy material having a suitable melting point may be used. The term "waxy material" is used herein in its broadest sense, and includes, but is not limited to, to a material which melts into liquid form having low viscosity upon heating and sets again to a crystalline solid state upon cooling. Such waxy materials include, without limitation, paraffinic waxes, microcrystalline waxes, animal waxes, vegetable waxes, substantially water-insoluble polymers, saturated fatty acids and fatty alcohols having from 12 to 40 carbon atoms in their alkyl chain, fatty esters such as fatty acid triglycerides, and fatty acid esters of sorbitan and fatty acid esters of fatty alcohols. Specific suitable waxy materials may be derived from compounds including lauric, myristic, palmitic, stearic, arachidic and behenic acids, stearyl and behenyl alcohol, microcrystalline wax, beeswax, spermaceti wax, candelilla wax, sorbitan tristearate, sorbitan tetralaurate, tripalmitin, trimyristin and octacosane, and stearyl alcohol.

In other preferred embodiments, the encapsulant is a water insoluble polymer. Examples of suitable water-insoluble polymeric materials include, but are not limited to, cellulose ethers such as ethyl, propyl or butyl cellulose; cellulose esters such as cellulose acetate, propionate, butyrate or acetate-butyrate; ureaformaldehyde resins, polyvinyl chloride, polyvinylidene chloride, polyethylene, polypropylene, polyacrylates, polymethacrylates, polymethyl-methacrylates and nylon. Such materials and their equivalents are described in greater detail in any handbook of synthetic organic plastics, for example, in *Modern Plastics Encyclopaedia*, Vol. 62, No. 10A (for 1985-1986) at pages

768-787, published by McGraw-Hill, New York, N.Y. (Oct. 1985), incorporated herein by reference in its entirety. A preferred polymeric material is ethyl cellulose. The polymeric coating materials can be plasticized with known plasticizing agents such as phthalate esters, adipate esters, sebacate esters, polyols (e.g., ethylene glycol), tricresyl phosphate, castor oil, and camphor. A preferred polymeric material is ethyl cellulose.

In other preferred embodiments, the encapsulant is a water soluble polymer. Examples of suitable synthetic water soluble polymers include, but are not limited to, polyvinyl pyrrolidone, water soluble celluloses, polyvinyl alcohol, ethylene maleic anhydride copolymer, methyl vinyl ether maleic anhydride copolymer, polyethylene oxides, water soluble polyamide or polyester, copolymers or homopolymers of acrylic acid such as polyacrylic acid, polystyrene acrylic acid copolymers, and mixtures thereof. Other suitable water soluble polymers include water-soluble hydroxyalkyl celluloses and carboxyalkyl celluloses, such as hydroxyethyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, carboxyethyl cellulose, hydroxymethyl cellulose, carboxymethyl cellulose, hydroxypropyl carboxymethyl cellulose, hydroxypropyl methyl carboxyethyl cellulose, hydroxypropyl carboxypropyl cellulose, hydroxybutyl carboxymethyl cellulose, alkali metal salts of these carboxyalkyl celluloses, such as sodium and potassium salts, and the like. Examples of water soluble natural and modified natural polymers include starch, gums, and gelatin. Modified starch in its various forms, including dextrans, may be also be suitable, as well as hydrolyzed gums and hydrolyzed gelatin. Hydrolyzed gums suitable for use as encapsulants include gum arabic, larch, pectin, tragacanth, locust bean, guar, alginates, carrageenans, cellulose gums such as carboxy methyl cellulose and karaya. Suitable modified starches typically have a dextrose equivalent of 0.25 up to about 20, preferably 5 to 15. Starch hydrolysates having dextrose equivalents of up to 95 are also useful, e.g., maltodextrins and dextrans and other starches are derived from corn, waxy maize, tapioca, and the like.

Microcapsules may be prepared using the M-CAP Process of Insulation Technologies Corporation of Darby, Pennsylvania. The M-CAP shell walls are microcapsules as small as three microns with melt temperatures of from about 20°C to 350°C. Microcapsules with varied melt temperatures can be included in a single cigarette to ensure a constant release of menthol as the coal burns down the tobacco rod. Where the rate control is designed to vary, the shell material, thickness or microcapsule size can be

accordingly varied. The M-CAP construction provides for uniform microcapsule size and for microcapsules smaller than fifty microns.

Microcapsules may be prepared using ethylene/vinyl acetate copolymers or a similar cellulite material having the desired characteristics of a programmable shell wall release temperature of between 20°C to 350°C. ELVAX™ is an ethylene vinyl acetate resin available from E. I. DuPont de Nemours & Co. of Wilmington, Del. Other suitable shell materials include EUDRAGIT E™ manufactured by Röhm America of Piscataway, N.J., which is a cationic copolymer synthesized from dimethylaminoethyl methacrylate and neutral methacrylic acid ester, and can form a rapidly disintegrating film coating; BERMOCOLL™, which is an ethylhydroxy ethylcellulose manufactured by Berol Kemi AB of Stenungsund, Sweden; K & K Gelatin, which is a gelatin manufactured by Kind & Knox, which is a division of Knox Gelatine, Inc., of Saddle Brook, N.J.; N-LOK™, which is an emulsion stabilizing material produced by National Starch and Chemical Corporation, Food Products Division, of Bridgewater, N.J.; and CAPSUL™, a modified starch also manufactured by National Starch. CAPSUL is made from waxy maize, and is especially suited for encapsulation and has an excellent shelf-life stability.

In preferred embodiment, the shell wall may make up from less than about 20% to more than about 50% of the microcapsule's volume for stability and durability. The microcapsules are preferably less than 10 µm in diameter so as not to be visible on the cut tobacco. However larger diameters may be preferred in certain embodiments. The microcapsules can be further hardened with a plasticizer to control their melt temperatures. The microcapsules can be dyed with suitable food dyes to match the color of the cigarette tobacco. In certain embodiments, double encapsulation or more may be desirable, depending upon the flavorant to be encapsulated.

In certain applications it may be preferred to use a shell material that decomposes or dissolves, for example, in the presence of water vapor in tobacco smoke, thereby releasing the encapsulated flavorant. In certain applications it may also be preferred to use a shell material that releases the enclosed encapsulant upon pyrolysis of the smoking material.

Suitable shell materials include, but are not limited to, gum arabic, gelatin, diethylcellulose, maltodextrins, and hydrogenated vegetable oils. Gelatin is particularly preferred because of its low cost and the ease with which gelatin shell microcapsules may be prepared. In certain embodiments, however, other shell materials may be preferred. The

optimum shell material may depend upon the particle size and particle size distribution of the filling material, the shape of the filling material particles, compatibility with the filling material, stability of the filling material, and the timing of the release of the filling material from the microcapsule.

Microencapsulation Processes

A variety of encapsulation methods may be used to prepare the microcapsules of preferred embodiments. These methods include gas phase or vacuum processes wherein a coating is sprayed or otherwise deposited on the filler material particles so as to form a shell, or wherein a liquid is sprayed into a gas phase and is subsequently solidified to produce microcapsules. Suitable methods also include emulsion and dispersion methods wherein the microcapsules are formed in the liquid phase in a reactor.

Spray Drying

Encapsulation by spray drying involves spraying a concentrated solution of shell material containing filler material particles or a dispersion of immiscible liquid filler material into a heated chamber where rapid desolvation occurs. Any suitable solvent system may be used. However, the method is most preferred for use with aqueous systems. Spray drying is commonly used to prepare microcapsules including shell materials such as, for example, gelatin, hydrolyzed gelatin, gum arabic, modified starch, maltodextrins, sucrose, or sorbitol. When an aqueous solution of shell material is used, the filler material typically includes a hydrophobic liquid or water-immiscible oil. Dispersants and/or emulsifiers may be added to the concentrated solution of shell material. Relatively small microcapsules may be prepared by spray drying methods, e.g., from less than about 1 μm to greater than about 50 μm . The resulting particles may include individual particles as well as aggregates of individual particles. The amount of filler material that may be encapsulated using spray drying techniques is typically from less than about 20 wt. % of the microcapsule to more than 60 wt. % of the microcapsule. The process is preferred because of its low cost compared to other methods, and has wide utility in preparing food grade microcapsules. The method may not be preferred for preparing heat sensitive materials, however.

In another variety of spray drying, chilled air rather than desolvation is used to solidify a molten mixture of shell material containing filler material in the form of particles or an immiscible liquid. Various fats, waxes, fatty alcohols, and fatty acids are typically

used as shell materials in such an encapsulation method. The method is generally preferred for preparing microcapsules having water-insoluble shells.

Fluidized-Bed Microencapsulation

Encapsulation using fluidized bed technology involves spraying a liquid shell material, generally in solution or melted form, onto solid particles suspended in a stream of gas, typically heated air, and the particles thus encapsulated are subsequently cooled. Shell materials commonly used include, but are not limited to, colloids, solvent-soluble polymers, and sugars. The shell material may be applied to the particles from the top of the reactor, or may be applied as a spray from the bottom of the reactor, e.g., as in the Wurster process. The particles are maintained in the reactor until a desired shell thickness is achieved. Fluidized bed microencapsulation is commonly used for preparing encapsulated water-soluble food ingredients and pharmaceutical compositions. The method is particularly suitable for coating irregularly shaped particles. Fluidized bed encapsulation is typically used to prepare microcapsules larger than about 100 μm , however smaller microcapsules may also be prepared.

Complex Coacervation

A pair of oppositely charged polyelectrolytes capable of forming a liquid complex coacervate (namely, a mass of colloidal particles that are bound together by electrostatic attraction) can be used to form microcapsules by complex coacervation. A preferred polyanion is gelatin, which is capable of forming complexes with a variety of polyanions. Typical polyanions include gum arabic, polyphosphate, polyacrylic acid, and alginate. Complex coacervation is used primarily to encapsulate water-immiscible liquids or water-insoluble solids. The method is generally not suitable for use with water soluble substances, or substances sensitive to acidic conditions.

In the complex coacervation of gelatin with gum arabic, a water insoluble filler material is dispersed in a warm aqueous gelatin emulsion, then gum arabic and water are added to this emulsion. The pH of the aqueous phase is adjusted to slightly acidic, thereby forming the complex coacervate which adsorbs on the surface of the filler material. The system is cooled, and a cross-linking agent, such as glutaraldehyde, is added. The microcapsules may optionally be treated with urea and formaldehyde at low pH so as to reduce the hydrophilicity of the shell, thereby facilitating drying without excessive aggregate formation. The resulting microcapsules may then be dried to form a powder.

Polymer-Polymer Incompatibility

Microcapsules may be prepared using a solution containing two liquid polymers that are incompatible, but soluble in a common solvent. One of the polymers is preferentially absorbed by the filler material. When the filler material is dispersed in the solution, it is spontaneously coated by a thin film of the polymer that is preferentially absorbed. The microcapsules are obtained by either crosslinking the absorbed polymer or by adding a nonsolvent for the polymer to the solution. The liquids are then removed to obtain the microcapsules in the form of a dry powder.

Polymer-polymer incompatibility encapsulation can be carried out in aqueous or nonaqueous media. It is typically used for preparing microcapsules containing polar solids with limited water solubility. Suitable shell materials include ethylcellulose, polylactide, and lactide-glycolide copolymers. Polymer-polymer incompatibility encapsulation is often preferred for encapsulating oral and parenteral pharmaceutical compositions, especially those containing proteins or polypeptides, because biodegradable microcapsules may be easily prepared. Microcapsules prepared by polymer-polymer incompatibility encapsulation tend to be smaller than microcapsules prepared by other methods, and typically have diameters of 100 μm or less.

Interfacial Polymerization

Microcapsules may be prepared by conducting polymerization reactions at interfaces in a liquid. In one such type of microencapsulation method, a dispersion of two immiscible liquids is prepared. The dispersed phase forms the filler material. Each phase contains a separate reactant, the reactants capable of undergoing a polymerization reaction to form a shell. The reactant in the dispersed phase and the reactant in a continuous phase react at the interface between the dispersed phase and the continuous phase to form a shell. The reactant in the continuous phase is typically conducted to the interface by a diffusion process. Once reaction is initiated, the shell eventually becomes a barrier to diffusion and thereby limits the rate of the interfacial polymerization reaction. This may affect the morphology and uniformity of thickness of the shell. Dispersants may be added to the continuous phase. The dispersed phase can include an aqueous or a nonaqueous solvent. The continuous phase is selected to be immiscible in the dispersed phase.

Typical polymerization reactants may include acid chlorides or isocyanates, which are capable of undergoing a polymerization reaction with amines or alcohols. The amine or

alcohol is solubilized in the aqueous phase in a nonaqueous phase capable solubilizing the amine or alcohol. The acid chloride or isocyanate is then dissolved in the water-immiscible or nonaqueous solvent-immiscible phase. Similarly, solid particles containing reactants or having reactants coated on the surface may be dispersed in a liquid in which the solid particles are not substantially soluble. The reactants in or on the solid particles then react with reactants in the continuous phase to form a shell.

In another type of microencapsulation by interfacial polymerization, commonly referred to as *in situ* encapsulation, a filler material in the form of substantially insoluble particles or in the form of a water immiscible liquid is dispersed in an aqueous phase. The aqueous phase contains urea, melamine, water-soluble urea-formaldehyde condensate, or water-soluble urea-melamine condensate. To form a shell encapsulating the filler material, formaldehyde is added to the aqueous phase, which is heated and acidified. A condensation product then deposits on the surface of the dispersed core material as the polymerization reaction progresses. Unlike the interfacial polymerization reaction described above, the method may be suitable for use with sensitive filler materials since reactive agents do not have to be dissolved in the filler material. In a related *in situ* polymerization method, a water-immiscible liquid or solid containing a water-immiscible vinyl monomer and vinyl monomer initiator is dispersed in an aqueous phase. Polymerization is initiated by heating and a vinyl shell is produced at the interface with the aqueous phase.

Gas Phase Polymerization

Microcapsules may be prepared by exposing filler material particles to a gas capable of undergoing polymerization on the surface of the particles. In one such method, the gas comprises p-xylene dimers that polymerize on the surface of the particle to form a poly(p-xylene) shell. Specialized coating equipment may be necessary for conducting such coating methods, making the method more expensive than certain liquid phase encapsulation methods. Also, the filler material to be encapsulated is preferably not sensitive to the reactants and reaction conditions.

Solvent Evaporation

Microcapsules may be prepared by removing a volatile solvent from an emulsion of two immiscible liquids, e.g., an oil-in-water, oil-in-oil, or water-in-oil-in-water emulsion. The material that forms the shell is soluble in the volatile solvent. The filler material is dissolved, dispersed, or emulsified in the solution. Suitable solvents include methylene

chloride and ethyl acetate. Solvent evaporation is a preferred method for encapsulating water soluble filler materials, for example, polypeptides. When such water soluble components are to be encapsulated, a thickening agent is typically added to the aqueous phase, then the solution is cooled to gel the aqueous phase before the solvent is removed. Dispersing agents may also be added to the emulsion prior to solvent removal. Solvent is typically removed by evaporation at atmospheric or reduced pressure. Microcapsules less than 1 μm or over 1000 μm in diameter may be prepared using solvent evaporation methods.

Centrifugal Force Encapsulation

Microencapsulation by centrifugal force typically utilizes a perforated cup containing an emulsion of shell and filler material. The cup is immersed in an oil bath and spun at a fixed rate, whereby droplets including the shell and filler material form in the oil outside the spinning cup. The droplets are gelled by cooling to yield oil-loaded particles that may be subsequently dried. The microcapsules thus produced are generally relatively large. In another variation of centrifugal force encapsulation referred to as rotational suspension separation, a mixture of filler material particles and either molten shell or a solution of shell material is fed onto a rotating disk. Coated particles are flung off the edge of the disk, where they are gelled or desolvated and collected.

Submerged Nozzle Encapsulation

Microencapsulation by submerged nozzle generally involves spraying a liquid mixture of shell and filler material through a nozzle into a stream of carrier fluid. The resulting droplets are gelled and cooled. The microcapsules thus produced are generally relatively large.

Desolvation

In desolvation or extractive drying, a dispersion filler material in a concentrated shell material solution or dispersion is atomized into a desolvation solvent, typically a water-miscible alcohol when an aqueous dispersion is used. Water-soluble shell materials are typically used, including maltodextrins, sugars, and gums. Preferred desolvation solvents include water-miscible alcohols such as 2-propanol or polyglycols. The resulting microcapsules do not have a distinct filler material phase. Microcapsules thus produced typically contain less than about 15 wt. % filler material, but in certain embodiments may contain more filler material.

Liposomes

Liposomes are microparticles typically ranging in size from less than about 30 nm to greater than 1 mm. They consist of a bilayer of phospholipid encapsulating an aqueous space. The lipid molecules arrange themselves by exposing their polar head groups toward the aqueous phase, and the hydrophobic hydrocarbon groups adhere together in the bilayer forming close concentric lipid leaflets separating aqueous regions. Flavorants can either be encapsulated in the aqueous space or entrapped between the lipid bilayers. Where the flavorant is encapsulated depends upon its chemical characteristics and the composition of the lipid.

Miscellaneous Microencapsulation Processes

While the microencapsulation methods described above are generally preferred for preparing the microcapsules of preferred embodiments, other suitable microencapsulation methods may also be used, as are known to those of skill in the art. Moreover, in certain embodiments, in addition to the encapsulated material, it may be desired to incorporate an unencapsulated flavorant or other substance directly on the smoking material, the filter materials, wrapping paper, or other components of the smoking article. The microcapsules added to the smoking material may all be of the same type and contain the same flavorants or other substances, or may include a variety of types and/or encapsulated flavorants or other substances.

Smokable Articles Containing Microencapsulated Flavorants

Microcapsules containing one or more flavorants or other substances are prepared as described above. To ensure that premature release of the flavorant does not occur upon addition of the microcapsules, it is desirable to ensure that the microcapsules are thoroughly dried and do not contact any substance that may negatively impact the integrity of the microcapsule shell.

The microcapsules may be incorporated into the smoking article in any convenient manner and at any convenient time in the fabrication process. In preferred embodiments, the microcapsules containing the flavorant are deposited onto the smokable material, for example, cut tobacco. The microcapsules may be added to the smokable material as part of the casing solution if the microcapsules will not degrade or melt in the presence of the solution. Alternatively, the microcapsules may be added to the smokable material in a separate step from the addition of other components. The microcapsules are preferably

added to the smokable material at a point in the fabrication process of the smoking article such that no subsequent processing steps are conducted that may result in the exposure of the microcapsules to conditions resulting in premature release of the flavorant.

The microcapsules may be added to the smokable material in pure form, for example, as a powder. Alternatively, the microcapsules may be applied as a suspension in a suitable liquid. The microcapsules or suspension of microcapsules may also contain a material to facilitate adhesion of the microcapsules to the smokable material. Suitable materials include gelatin or other viscous materials as are known in the art. In order to form a homogenous mixture of microcapsules and liquid carrier or other components, any suitable mixing method may be used, for example, mechanical stirring, shaking, or sonication. It is preferred that the mixing method not result in substantial damage of the microcapsules and the resulting premature release of flavorant or other substances contained therein. Preferably, the components are mixed and stored under an inert atmosphere or sealed in an airtight container prior to application.

The microcapsules are typically added to the smokable material to provide a concentration of flavorant of from less than about 0.001, 0.005, or 0.01 wt. % flavorant to more than about 3, 4, or 5 wt. % flavorant on a tobacco weight basis, preferably from about 0.05, 0.1, or 0.2 wt. % to about 1, 1.5, 2, or 2.5 wt. %, and more preferably from about 0.3, 0.4, or 0.5 wt. % to about 0.6, 0.7, 0.8 or 0.9 wt. %. The optimal concentration may depend upon the concentration of flavorant material in the microcapsules, the type of flavorant or flavorants used, the desired release rate and level of the flavorant, the encapsulating material, and the method of encapsulation used to prepare the flavorant microcapsules.

In certain embodiments, it may be preferred to incorporate the microcapsules into a portion of the smoking article other than the cut tobacco or other smokable material, for example, in one or more of the filter materials, in a cartridge contained within the filter or tobacco rod, or any other location, as will be appreciated by one skilled in the art.

Catalyst System for Reducing Carcinogens in Smoke

In preferred embodiments, smoking articles incorporating the microencapsulated flavorant also incorporate a catalyst system including catalytic metallic and/or carbonaceous particles and a nitrate or nitrite source. The catalyst system is incorporated into the smokable material so as to reduce the concentration of certain undesirable components in the resulting smoke. In embodiments wherein the particles are metallic, the

particles are preferably prepared by heating an aqueous solution of a metal ion source and a reducing agent, preferably a reducing sugar or a metal ion source with hydroxide. Preferably, after the metallic particles are formed in solution, the nitrate or nitrite source is added to the solution, and the solution is applied to the smokable material. However, embodiments in which the particles and the nitrate or nitrite source are added separately to the smokable material are also contemplated. The catalyst system and smoking articles incorporating the same are described in detail in copending U.S. Application No. 10/007,724 filed November 9, 2001 and entitled "METHOD AND PRODUCT FOR REMOVING CARCINOGENS FROM TOBACCO SMOKE," the contents of which is incorporated herein by reference in its entirety.

Metallic Particles

In preferred embodiments, particles of a catalytic metallic substance are applied to the smokable materials. The term "metallic," as used herein, is a broad term and is used in its ordinary sense, including without limitations, pure metals, mixtures of two or more metals, mixtures of metals and non-metals, metal oxides, metal alloys, mixtures or combinations of any of the aforementioned materials, and other substances containing at least one metal. Suitable catalytic metals include the transition metals, metals in the main group, and their oxides. Many metals are effective in this process, but preferred metals include, for example, Pd, Pt, Rh, Ag, Au, Ni, Co, and Cu.

Many transition and main group metal oxides are effective, but preferred metal oxides include, for example, AgO, ZnO, and Fe₂O₃. Zinc oxide and iron oxide are particularly preferred based on physical characteristics, cost, and carcinogenic behavior of the oxide. A single metal or metal oxide may be preferred, or a combination of two or more metals or metal oxides may be preferred. The combination may include a mixture of particles each having different metal or metal oxide compositions. Alternatively, the particles themselves may contain more than one metal or metal oxide. Suitable particles may include alloys of two or more different kinds of metals, or mixtures or alloys of metals and nonmetals. Suitable particles may also include particles having a metal core with a layer of the corresponding metal oxide making up the surface of the particle. The metallic particles may also include metal or metal oxide particles on a suitable support material, for example, a silica or alumina support. Alternatively, the metallic particles may include particles including a core of support material substantially encompassed by a layer of

catalytically active metal or metal oxide. In addition to the above-mentioned configurations, the metallic particles may in any other suitable form, provided that the metallic particles have the preferred average particle size.

The particles may be prepared by any suitable method as is known in the art. When preparing metallic particles, suitable methods include, but are not limited to, wire electrical explosion, high energy ball milling, plasma methods, evaporation and condensation methods, and the like. However, in preferred embodiments, the particles are prepared via reduction of metal ions in aqueous solution, as described below.

While any suitable metal, metal oxide, or carbonaceous particle (as described below) is preferred, it is particularly preferred to use a metal, metal oxide, or carbonaceous particle that has a relatively low level of transfer to cigarette or other smoke condensate produced upon combustion of the smokable material. For example, palladium has a lower level of transfer than silver. Also, metal oxides tend to have relatively low levels of transfer. However, in certain embodiments it may be preferred to use a metal, metal oxide, or carbonaceous particle having a relatively high level of transfer to smoke condensate. In providing a compound that effectively catalyzes the decomposition of nitrate salts, it is also generally preferred that the metal, metal oxide, or carbonaceous particle have a relatively low specific heat.

Carbonaceous Particles

In certain embodiments, particles of a catalytic carbonaceous substance are applied to the smokable materials. The term "carbonaceous", as used herein, is a broad term and is used in its ordinary sense, including without limitations, graphitic carbon, fullerenes, doped fullerenes, carbon nanotubes, doped carbon nanotubes, other suitable carbon-containing substances, and mixtures or combinations of any of the aforementioned substances.

The carbonaceous particles may be prepared by any suitable method as is known in the art. When preparing graphitic particles suitable methods may include, but are not limited to, milling techniques, and the like.

Fullerenes include, but are not limited to, buckminster fullerene (C_{60}), as well as C_{70} and higher fullerenes. The structure of fullerenes and carbon nanotubes may permit them to be doped with other atoms, for example, metals such as the alkali metals, including potassium, rubidium and cesium. These other atoms may be included within the carbon cage or carbon nanotube, as is observed for certain atoms when enclosed within endohedral

fullerene. Atoms may also be incorporated into a crystal structure, e.g., the bct structure of A_4C_{60} (wherein $A=K,Rb,Cs$, and C =buckminster fullerene) or the bcc structure of A_6C_{60} (wherein $A=K,Rb,Cs$, and C =buckminster fullerene). Fullerenes may also be dimerized or polymerized. Certain fullerenes, such as C_{70} fullerenes, are known radical traps and as such may be suitable for use in a catalyst system without the presence of nitrate or other radical trap generators.

Fullerenes are preferably prepared by condensing gaseous carbon in an inert gas. The gaseous carbon is obtained, for example, by directing an intense pulse of laser at a graphite surface. The released carbon atoms are mixed with a stream of helium gas, where they combine to form clusters of carbon atoms. The gas containing clusters is then led into a vacuum chamber where it expands and is cooled to a few degrees above absolute zero. The clusters are then extracted. Other suitable methods for preparing fullerenes as are known in the art may also be used.

Carbon nanotubes may be prepared by electric arc discharge between two graphite electrodes. In the electric arc discharge method, material evaporates from one electrode and deposits on the other in the form of nanoparticles and nanotubes. Purification is achieved by competitive oxidation in either the gas or liquid phase. Carbon nanotubes may also be catalytically grown. In catalytic methods, filaments containing carbon nanotubes are grown on metal surfaces exposed to hydrocarbon gas at temperatures typically between 500-1100°C. Other techniques for forming carbon nanotubes include laser evaporation techniques, similar to those used to form fullerenes. However, any suitable method for forming carbon nanotubes may be used.

Particle Size

The particles of preferred embodiments preferably have an average particle size of greater than about 0.5 micron (0.5 μm), more preferably greater than about 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 2 μm . The preferred size may depend on the metallic or carbonaceous substance. Particle sizes can be as large as 150 μm or more, more preferably 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 19, 18, 17, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3 μm or less in diameter. In other embodiments, preferred particle size may be less than about 0.5 μm (500 nm), or 400, 300, 200, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 nm or less. In preferred embodiments, the particles are of a substantially uniform size distribution, that is, a majority of the

metallic particles present have a diameter generally within about $\pm 50\%$ or less of the average diameter, preferably within about $\pm 45\%$, 40% , 35% , 30% or less of the average diameter, more preferably within $\pm 25\%$ or less of the average diameter, and most preferably within $\pm 20\%$ or less of the average diameter. The term "average" includes both the mean and the mode.

While a uniform size distribution may be generally preferred, individual particles having diameters above or below the preferred range may be present, and may even constitute the majority of the particles present, provided that a substantial amount of particles having diameters in the preferred range are present. In other embodiments, it may be desirable that the particles constitute a mixture of two or more particle size distributions, for example, a portion of the mixture may include a distribution on nanometer-sized particles and a portion of the mixture may include a distribution of micron-sized particles. The particles of preferred embodiments may have different forms. For example, a particle may constitute a single, integrated particle not adhered to or physically or chemically attached to another particle. Alternatively, a particle may constitute two or more agglomerated or clustered smaller particles that are held together by physical or chemical attractions or bonds to form a single larger particle. The particles may have different atomic level structures, including but not limited to, for example, crystalline, amorphous, and combinations thereof. In various embodiments, it may be desirable to include different combinations of particles having various properties, including, but not limited to, particle size, shape or structure, chemical composition, crystallinity, and the like.

Nitrate or Nitrite Source

Any suitable source of nitrate or nitrite may be preferred. Preferred nitrate or nitrite sources include the nitrate or nitrite salts of metals selected from Groups Ia, Ib, IIa, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, and the transition metals of the Periodic Table of Elements.

In preferred embodiments, the nitrate or nitrite source includes a nitrate of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, yttrium, lanthanum, cerium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, erbium, scandium, manganese, iron, rhodium, palladium, copper, zinc, aluminum, gallium, tin, bismuth, hydrates thereof and mixtures thereof. Preferably, the nitrate salt may be an alkali or alkaline earth metal nitrate. More preferably, the nitrate or nitrite source may be selected from the group of calcium, magnesium, and zinc with magnesium nitrate being the most

preferred salt. In a particularly preferred embodiment, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ may be preferred as a nitrate source. While nitrate and nitrite salts are generally preferred, any suitable metal salt or organometallic compound, or other compound capable of releasing nitric oxide may be preferred.

While not wishing to be limited to any particular mechanism, it is believed that the nitrate or nitrite source forms nitric oxide radicals and that this reaction process is catalyzed by the metallic or carbonaceous particles in the combustion zone of tobacco. The nitric oxide radicals are believed to act as a trap for other organic radicals that are responsible for formation of PAHs and other carcinogenic compounds.

The temperature at which a particular nitrate or nitrite source decomposes to form nitric oxide may vary. Since a temperature gradient exists across the combustion zone of a tobacco rod, the choice and concentration of the nitrate or nitrite source may be selected so as to provide optimum production of nitric oxide during combustion. Certain nitrates and nitrites alone, especially those of the Group Ia metals, function as effective combustion promoters, accelerating the burn rate of the smokable material and decreasing the total smoke yield, but not necessarily decreasing the quantity of PAHs within the smoke. The nitric oxide yield of such nitrates may also be relatively low.

In certain embodiments, it may be preferred that the metal ion source and the nitrate or nitrite source constitute the same compound, for example, palladium(II) nitrate.

Catalyst Preparation

In preferred embodiments, metallic particles may be prepared from an aqueous solution. For example, metal particles may be prepared from an ion source containing one or more metal ion sources and one or more reducing sugars. Suitable metal ion sources include any ionic or organometallic compound that is soluble in aqueous solution and is capable of yielding metal ions that may be reduced to particles of a catalytic metal or utilized to form a metal oxide. In a particularly preferred embodiment, the catalytic source includes a metal such as palladium, and the palladium ion source includes water-soluble palladium salts. Illustrative non-limiting examples of suitable palladium salts include simple salts such as palladium nitrate, palladium halides such as palladium di or tetrachloride diammine complexes such as dichlorodiamminepalladium(II) ($\text{Pd}(\text{NH}_3)_2\text{Cl}_2$), and palladate salts, especially ammonium salts such as ammonium tetrachloropalladate(II) and ammonium hexachloropalladate(IV).

One form of palladium that may be especially preferred is ammonium tetrachloropalladate(II), $(\text{NH}_4)_2\text{PdCl}_4$. Ammonium tetrachloropalladate is generally preferred over ammonium hexachloropalladate because under typical conditions for preparing the metallic particles, a higher metal ion to metal conversion may be observed for ammonium tetrachloropalladate(II).

In a preferred embodiment, an aqueous solution of reducing agent is prepared, to which the metal ion source is added. In preferred embodiments, the reducing agent may be a reducing sugar, however other suitable reducing agents may be preferred. Although any compound capable of reducing the metal ion can be employed, as a practical matter the reducing agent is preferably non-toxic and preferably does not form toxic byproducts when pyrolyzed during smoking. In addition, the reducing agent is preferably water-soluble.

Preferred reducing agents are the reducing sugars, including organic aldehydes, including hydroxyl-containing aldehydes such as the sugars, for example glucose, mannose, galactose, xylose, ribose, and arabinose. Other sugars containing hemiacetal or keto groupings may be employed, for example, maltose, sucrose, lactose, fructose, and sorbose. Pure sugars may be employed, but crude sugars and syrups such as honey, corn syrup, invert syrup or sugar, and the like may also be employed. Other reducing agents include alcohols, preferably polyhydric alcohols, such as glycerol, sorbitol, glycols, especially ethylene glycol and propylene glycol, and polyglycols such as polyethylene and polypropylene glycols. In alternative embodiments, other reducing agents may be preferred such as carbon monoxide, hydrogen, or ethylene.

The solution is preferably heated before the metal ion source is added to the solution, and maintained at an elevated temperature afterwards so as to reduce the time for conversion of the metal ions to metallic particles. In a preferred embodiment, a reducing sugar such as low invert sugar may be preferred as the reducing agent. In certain embodiments, it may be desirable to have an excess or deficiency of reducing agent present in solution. Generally, it is preferred to prepare an aqueous solution containing from about 5 wt. % to about 20 wt. % of the reducing sugar, preferably about 6 wt. % to about 16 or 17 wt. %, more preferably from about 7, 8, 9, 10, or 11 wt. % to about 12, 13, 14, or 15 wt. %. When the reducing agent is invert sugar, it is preferred to prepare a 11 wt. % to about 12 wt. % solution. The amount of reducing agent preferred may vary depending on the type of reducing agent preferred and the amount of metal ion source to be added to the solution.

It may be preferred to prepare the solution in a glass-lined vessel equipped with a heating jacket. In certain embodiments, however, it may be preferred to prepare the solution in another kind of vessel constructed of or lined with another type of material, for example, plastic, stainless steel, ceramic, and the like. It is generally preferred to conduct the reaction in a closed vessel. In certain embodiments, it may be desirable to conduct the reaction under reduced pressure or elevated pressure, or under an inert atmosphere, such as nitrogen or argon.

In preparing the aqueous solution of the reducing sugar, it is preferred to use deionized ultrafiltered water. While in preferred embodiments the metallic particles are prepared from aqueous solution, in other embodiments it may be desirable to use another suitable solvent system, for example, a polar solvent such as ethanol, or a mixture of ethanol and water. Additional components may be present in the solution as well, provided that they do not substantially adversely impact the catalytic activity of the metallic particles.

After adding the reducing sugar to the deionized ultrafiltered water, the solution is preferably heated with constant mixing so as to avoid hot spots in the solution. Although in certain embodiments it may be desirable to prepare the particles from a room temperature solution, or even a solution cooled below room temperature, it is generally preferred to heat the solution so as to speed the reaction between the reducing sugar and the metal ion source once it is added to the solution. The solution may be heated to any suitable temperature, but boiling of the solution and decomposition of the reducing sugar is preferably avoided. In a preferred embodiment wherein low invert sugar is the reducing sugar, the solution is typically heated up to about 95°C or more, preferably from above room temperature to about 90°C, more preferably from about 50°C, 55°C, 60°C, or 65°C to about 85°C, and most preferably from about 70°C or 75°C to about 80°C.

The metal ion source is added to the heated aqueous solution of reducing agent, which is stirred while the metal ions react with the reducing sugar to produce metallic particles. It is generally preferred to add sufficient metal ion source so as to produce a solution containing from less than about 3000 ppm to more than about 5000 ppm metal. Preferably, sufficient metal ion source is added to produce a solution containing from about 3250, 3500, or 3750 ppm to about 4250, 4500, 4750 ppm metal, more preferably from about 3800, 3850, 3900, or 3950 ppm to about 4050, 4100, 4150, or 4200 ppm metal, and most preferably about 4000 ppm metal.

The reaction time for conversion of metal ion to metal particles may vary depending upon the reducing agent and metal ion source preferred, but generally ranges from about 30 minutes or less to about 24 hours or more, and typically ranges from about 1 or 2 hours up to about 3, 4, or 5 hours. In a preferred embodiment, wherein ammonium tetrachloropalladate is the metal ion source, a substantial conversion of palladium ion to palladium metal may be achieved after 3 hours for a solution heated to a temperature of about 75°C. Although in certain embodiments a lower conversion may be acceptable, it is generally desirable to achieve a conversion of metal ion to metal of at least 50%, preferably at least 60%, more preferably at least 70%, and most preferably at least 75, 80, 85% or more.

The metallic particles produced in this manner generally have diameters of about 1 μm or less. In certain other embodiments metallic particles having individual diameters and average diameters below about 20 nm or above about 1 μm may be produced. The size of the metallic particles may be conveniently determined using conventional methods of X-ray diffraction or other particle size determination methods, for example, laser scattering.

After a sufficient conversion of metal ion to metal or metal oxide is achieved, and the metallic particles are formed, the nitrate or nitrite source is added to the suspension. Any suitable compound that yields nitrate or nitrite ion in aqueous solution may be preferred. Preferably, the nitrate or nitrite source is an alkali metal or alkaline earth metal nitrate or nitrite. In a particularly preferred embodiment, the nitrate or nitrite source is magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. It is generally preferred to add a sufficient amount of nitrate or nitrite source so as to produce a solution containing from less than about 70 ppm to more than about 100 ppm nitrogen (in the form of nitrate or nitrite). Preferably, sufficient nitrate or nitrite source is added to produce a solution containing from about 75, 80, or 85 ppm to about 90 or 95 ppm nitrogen, more preferably from about 80 ppm nitrogen.

Generally, it is preferred that the suspension of metallic particles not be excessively concentrated or dilute, so as to facilitate efficient application of the suspension to the smokable material.

While it is generally preferred to prepare a suspension of particles as described above by reduction of metal ion in solution, followed by addition of the nitrate or nitrite source, in other embodiments it may be preferred to use a different method to prepare the

particles. If the metallic or carbonaceous particles are not prepared in solution, the particles may be mixed with an appropriate liquid to form a suspension. Because of their high surface area, it may be difficult to sufficiently wet the surface of the particles so as to form a uniform suspension. In such cases, any suitable method may be preferred to facilitate forming the suspension, including, but not limited to, mechanical methods such as sonication or heating, or chemical methods such as the use of small quantities of surfactants, provided the surfactants do not interfere with the catalytic activity of the particles. Once the suspension is formed, addition of the nitrate or nitrite source may proceed as described above.

While it is generally preferred to apply the metallic or carbonaceous particles and nitrate or nitrite source to the smokable material in the form of a suspension, other methods of applying the particles and nitrate or nitrite source are also contemplated. For example, if the particles are in dry form, they may be added to the smokable material as a powder. It may be advantageous to moisten the smokable material with a suitable substance, for example, water, prior to application of the powder in order to provide better adhesion of the particles to the smokable material.

When the carbonaceous or metallic particles are added to the smokable material in powder form, the nitrate or nitrite source in solid form may also be applied to the smokable material in powder form, either in a separate step before or after the addition of the particles, or simultaneously with the particles, for example, in admixture with the particles. Suitable methods as are well known in the art may be used to prepare a suitable solid form of nitrate or nitrite source. In particularly preferred methods, the solid form of nitrate or nitrite source is prepared by freeze drying or spray drying methods, both of which may yield extremely small particle sizes. It is generally preferred that the nitrate or nitrite source be in the form of particles having an average diameter on the order of the preferred average diameters for the particles. The nitrate or nitrite source may also be provided as a solution applied to the smokable material as a separate step from adding the particle powder, preferably before adding the particle in dry form to the smokable material.

Optimization of the Catalyst System

There are many aspects to consider when attempting to optimize the catalyst system, the first of which is the conversion of the palladium salt to palladium metal in the aqueous reducing solution. This conversion requires a chemical reduction reaction in an aqueous

solution. Earlier work was directed to the conversion of the palladium salt to palladium metal in a casing solution. It was suggested from the patent literature that the reducing agent for this reaction in the casing solution was fructose - a known reducing sugar. One origin of fructose in the casing solution is from low invert sugar. In order to try to repeat this earlier research with casing solutions and produce a more consistent/controllable reaction, all of the components in the casing solution were eliminated that were considered non-essential to the reduction reaction (e.g. propylene glycol, licorice, cocoa, and the like), while the components thought to be essential (e.g. water, palladium salt and low invert sugar) were retained in the same ratios as found in the casing solution, namely 93 g water to 1 g palladium salt to 8 g low invert sugar per pound of tobacco, respectively. Another component that was in the original casing solution but is considered non-essential to the reduction reaction was $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. This component was present in early formulations, however nitrate analysis of the tobacco verified that $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ decomposes to a certain degree when mixed in aqueous solutions containing palladium metal. It was also found through early testing that carcinogen reduction in cigarettes was not reproducible when the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was allowed to be in contact with palladium metal for extended periods of time. Upon removal of the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from the reacting solution, and instead the addition of it prior to catalyst application on the tobacco, consistent and reproducible carcinogen reductions in experimental cigarettes were obtainable.

One feature of the preferred reduction reaction is the percent conversion of palladium salt to palladium metal in the aqueous solution containing low invert sugar as a reducing agent. At a temperature of approximately 70-75°C, the percent conversion typically increases steadily with time and after the first three hours of the reaction more than 60-70% of the salt has typically been converted to the metal. Most of the palladium salt is typically converted to metal within the first hour (approximately 50%). Longer reaction times (for example, above three hours) generally only increase the percent conversion modestly. Given the task of balancing maximum conversion with an acceptable production schedule, three hours is generally preferred as the minimum time for this reaction to occur before application of the catalyst solution to the tobacco.

To increase production rates and lower production costs, it is desirable to increase the percent conversion of palladium salt to palladium metal. An immediate benefit of

increasing the percent conversion is the capacity to use less total palladium salt in the reaction as an increase in percent conversion with less salt could in fact produce equivalent amounts of palladium metal in the reaction. This results in lower consumption of the most expensive reagent in the reaction.

Several possibilities exist to increase the percent conversion of this reaction. The reduction reaction is based on an aldehyde being oxidized and releasing electrons to the Pd II nucleus, thereby producing metallic palladium.



In a particularly preferred catalyst system as described above, it is believed that the aldehyde source is the reducing sugar fructose. In theory, any compound containing an aldehyde functional group can reduce the palladium salt to palladium metal, however to apply the resulting mixture to tobacco it is preferred that the reducing agent is non-toxic. As discussed previously in regard to the particularly preferred catalyst system, low invert sugar is used as the "reducing agent" for this reaction and it is believed that the fructose component of low invert sugar is the active reducing agent. Interestingly, pure fructose when supplied as a reducing agent for the palladium reduction has been shown not to be very effective, even when the fructose is in 10 molar excess. This observation suggests that there is an additional "co-reducing agent" or possibly a catalyst for the reducing agent contained within the low invert sugar solution. Due to the complex mixture associated with low invert sugar it will continue to be a challenge to discover exactly what the reducing agent or agents are when utilizing low invert sugar as a reactant. Nevertheless, the particularly preferred system performs remarkably well given the fact that the mechanism for palladium reduction is not well understood in this system.

Application of Catalyst to Smokable Material

After the nitrate or nitrite source has been added to the suspension containing metallic or carbonaceous particles, it is applied to the smokable material. If the smokable material is tobacco, it is preferred to apply the suspension to cut filler prior to addition of the top flavor. If a top flavor is not applied, then it is preferred to apply the suspension to the cut filler as a final step, for example, before it is formed into a tobacco rod. The catalytic particles may be applied before, during or after application of a casing solution, however in a preferred embodiment the catalytic particles are applied after application of

the casing solution. Casing solutions are pre-cutting solutions or sauces added to tobacco and are generally made up of a variety of ingredients, such as sugars and aromatic substances. Such casing solutions are generally added to tobacco in relatively large amounts, for example, one part casing solution to five parts tobacco.

The particles and nitrate or nitrite source are preferably well dispersed throughout the tobacco so as to provide uniform effectiveness throughout the entire mass of smokable material and throughout the entire period during which the material is smoked. In the case of cigarette tobacco wherein a blend of various tobaccos is preferred, the suspension may be applied to one or more of the blend constituents, or all of the blend constituents, as desired. Preferably, the suspension is applied to all of the blend constituents so as to ensure substantially uniform coverage of the particles and nitrate or nitrite source.

For certain types of suspensions of particles, a degradation in performance may be observed if an excessive period of time is allowed to elapse before the suspension is applied to the smokable product. This degradation in performance may be due to various factors, including loss of particles from the suspension due to their accumulation on the interior surfaces of the reaction vessel, or an undesirable increase in particle size over time. When the suspension includes palladium particles, the suspension is generally applied to the cut filler within about ten hours after the desired degree of metal ion conversion is reached and the nitrate or nitrite source is added to the suspension. The suspension is preferably applied within about 9, 8, 7, or fewer hours, more preferably within about 6, 5, or 4 hours, and most preferably within 3, 2, or 1 hours or less. However, in certain embodiments, including those utilizing palladium particles, it may be possible to apply the suspension after a delay of longer than ten hours while maintaining acceptable catalytic performance.

It is preferred to apply the suspension to the smokable material in the form of a fine mist, such as is produced using an atomizer. In a particularly preferred embodiment, the suspension is applied to tobacco, preferably cut filler, in a rotating tumbler equipped with multiple spray heads. Such a method of application ensures an even coating of the metallic particles on the tobacco product. The tobacco may be heated during or after application of the solution so as to facilitate evaporation of excess solvent.

It is preferred to add a sufficient quantity of the metallic or carbonaceous particle suspension to the smokable material such that the smokable material contains from about 500 ppm or less to about 1500 or more ppm of the metal or carbon in the form of catalytic

particles. Preferably, the smokable material contains from about 500 ppm to about 1000, 1100, 1200, 1300, or 1400 ppm of the metal or carbon in the form of catalytic particles, more preferably 500, 600 or 700 to about 800, 900, or 1000 ppm, and most preferably about 800 ppm. It is generally preferred that the smokable material contains from about 0.4 to about 1.5 wt. % nitrogen (from nitrate or nitrite). Preferably, the smokable material contains from about 0.5 or 0.6 wt. % to about 1.0, 1.1, 1.2, 1.3, or 1.4 wt. % nitrogen, more preferably from about 0.6, 0.7, or 0.8 wt. % to about 0.9 wt. %, and most preferably about 0.9 wt. % nitrogen. In a preferred embodiment, one kilogram of tobacco constitutes 800 milligrams of metal or carbon in the form of catalytic particles, and 9 grams of nitrogen in the form of the nitrate or nitrite source.

Once the metallic or carbonaceous particles and nitrate or nitrite source have been applied, the smokable material may be further processed and formed into any desired shape or used loosely, for example, in cigars, cigarettes, or pipe tobacco, in any suitable manner as is well-known to those skilled in the art.

The Filter

In preferred embodiments wherein the smokable material to which the microencapsulated flavorant has been applied is fashioned into a smokable article, a filter for the smokable article is provided. The filter can be provided in combination with cigarettes or cigars or other smokable devices containing divided tobacco or other smokable material. Preferably, the filter is secured to one end of the smokable article, positioned such that smoke produced from the smokable material passes into the filter before entering the smoker. Alternatively, the filter can be provided by itself, in a form suitable for attachment to a cigarette, cigar, pipe, or other smokable device utilizing the smokable material to which microencapsulated flavorant has been applied according to preferred embodiments.

The filter according to preferred embodiments advantageously removes at least one undesired component from tobacco smoke or the smoke of any other smokable material. Undesired components in tobacco smoke may include permanent gases, organic volatiles, semivolatiles, and nonvolatiles. Permanent gases (such as carbon dioxide) make up 80 percent of smoke, and are generally unaffected by filtration or adsorption materials. The levels of organic volatiles, semivolatiles, and nonvolatiles may be reduced by filters of various designs. The filters according to preferred embodiments may advantageously

remove undesired components including, but not limited to, tar, nicotine, carbon monoxide, nitrogen oxides, HCN, acrolein, nitrosamines, particulates, oils, various carcinogenic substances, and the like.

The filter preferably permits satisfactory or improved smoke flavor, nicotine content, and draw characteristics. The filter is preferably designed to be acceptable to the user, being neither cumbersome nor unattractive. Further, filters according to preferred embodiments may be made of inexpensive, safe and effective components, and may preferably be manufactured with standard cigarette manufacturing machinery.

The filter may incorporate one or more materials capable of absorbing, adsorbing, or reacting with at least one undesirable component of tobacco smoke. Such absorbing, adsorbing, or reacting materials may be incorporated into the filter using any suitable method or device. In a preferred embodiment, the absorbing, adsorbing, or reacting material may be contained within a smoke-permeable cartridge to be placed within the filter, or contained within a cavity within the filter. In another embodiment, the absorbing, adsorbing, or reacting material is deposited on and/or in the filter material.

Application methods may include forming a paste of the absorbing, adsorbing, or reacting material in a suitable liquid, applying the paste to the filter material, and allowing the liquid to evaporate. Alternatively, the absorbing, adsorbing, or reacting material may be mixed with an adhesive substance and applied to the filter material. All of the filter material may include the absorbing, adsorbing, or reacting material, or only a portion of the filter material may include the adsorbing or reacting material. The portion of the filter material containing the absorbing, adsorbing, or reacting material is generally referred to as a "a smoke-altering filter segment."

The cigarette filters of the preferred embodiments preferably include activated carbon (commonly referred to as charcoal) as an adsorbing material. The process by which activated carbon removes compounds is adsorption, which is a different process than absorption. Absorption is the process whereby absorbates are dispersed throughout a porous absorbent, while adsorption is a surface attraction effect. Both adsorption and absorption can be physical or chemical effects. The adsorptive effect associated with activated carbon is mainly a physical effect. In activated carbon filters, smoke compounds in the organic volatile and semivolatile phases diffuse through the carbon particles, move over the surface and then move into the activated carbon pores compelled by a phenomenon

known as Van der Waal's forces. Although these forces are generally considered weak, at very short range (one or two molecular diameters), they are strong enough to attract and effectively hold smoke components.

Activated carbon may be obtained from a variety of sources, including, but not limited to, wood, coconut shells, coal, and peat. Wood generally produces soft and macroporous activated carbon (pores from 50 to 1,000 nm in diameter). Peat and coal materials generally produce activated carbon that is predominantly mesoporous (pores 2 to 50 nanometers in diameter). Activated carbon derived from coconut shells is generally microporous (pores of less than 2 nm in diameter), has a large surface area, and has a low ash and base metal content when compared to certain other types of activated carbon.

Preferred activated carbons are microporous and have a high density, which imparts improved structural strength to the activated carbon so that it can resist excessive particle abrasion during handling and packaging.

The filters of preferred embodiments may also contain various other adsorptive, absorptive, or porous materials in addition to activated carbon as described above. Examples of such materials, include, but are not limited to, cellulosic fiber, for example, cellulose acetate, cotton, wood pulp, and paper; polymeric materials, for example, polyesters and polyolefins; ion exchange materials; natural and synthetic minerals such as activated alumina, silica gel, and magnesium silicate; natural and synthetic zeolites and molecular sieves (see, for example U.S. Patent No. 3,703,901 to Norman et al., incorporated herein by reference in its entirety); natural clays such as meerschaum; diatomaceous earth; activated charcoal and other materials as will be understood by those with skill in the art. The adsorptive, absorptive, or porous material may be any nontoxic material suitable for use in filters for smokable devices that are compatible with other substances in the smoking device or smoke to be filtered.

Typically, the filter element may include as the major component a porous material, for example, cellulose acetate tow or cellulosic paper, referred to below as a "filter material." The adsorptive or absorptive component, often a granular or particulate substance such as activated carbon, is generally dispersed within the porous filter material of the filter segment or positioned within a cartridge or cavity (for example, within a cavity of a triple filter, as discussed below).

The filter material may have the form of a non-woven web of fibers or a tow. Alternatively, the filter material may have a sheet-like form, particularly when the material is formed from a mixture of polymeric or natural fibers, such as cotton or wood pulp. Filter material in web or sheet-like form can be gathered, folded, crimped, or otherwise formed into a suitable (for example, cylindrical) configuration using techniques which will be apparent to one skilled in the art. See, for example, U.S. Pat. No. 4,807,809 to Pryor et al., which is incorporated herein by reference in its entirety.

In preferred embodiments, the filter material constitutes cellulose acetate tow or cellulose paper. Cellulose acetate tow is the most widely preferred filter material in cigarettes worldwide. Cellulose paper filter materials generally provide better tar and nicotine retention than do acetate filters with a comparable pressure drop, and have the added advantage of superior biodegradability. Cellulose and cellulose acetate reduce the amount of chemicals in the semivolatile phase and the nonvolatile phase, which is composed of solid particulates (commonly referred to as "tar"). These compounds are reduced in direct proportion to the amount of cellulose or cellulose acetate in the filter. Increasing density of the cellulose or cellulose acetate generally means increasing the pressure drop, which increases the filter retention and therefore decreases tar delivery. Filters retain generally less than 10 percent of vapor phase components.

In certain embodiments, it may be preferred to use a polymeric material such as cellulose acetate as the filter material rather than a material such as cellulose paper. Polymeric materials may be preferred in embodiments wherein superior chemical inertness or structural integrity during use are desired attributes of the filter, for example, when certain smoke altering components reactive to cellulose paper are present in the filter, or when components reactive to cellulose paper are generated within the filter. Cellulose acetate tow (such as that available from Celanese Acetate of Charlotte, NC) is the most commonly preferred polymeric material, however suitable polymeric materials may include other synthetic addition or condensation polymers, such as polyamides, polyesters, polypropylene, or polyethylene.

The polymeric material may be any nontoxic polymer suitable for use in filters for smokable devices that are compatible with other substances in the smoking device or smoke to be filtered, and which possess the desired degree of inertness. The polymeric material is preferably in fibrous tow form, but may optionally be in other physical forms,

for example, crimped sheet. The polymeric material may constitute a single polymer or a mixture of different polymers, for example, two or more of components such as homopolymers, copolymers, terpolymers, functionalized polymers, polymers having different molecular weights, polymers constituting different monomers, polymers constituting two or more of the same monomers in different proportions, oligomers, and nonpolymeric components. The polymer may also be subjected to suitable pre-treatment or post-treatment steps, for example, functionalization of the polymer, coating with suitable materials, and the like.

When polymeric fibers are the filter material, they can make up all or a portion of the composition of the filter material of the filter. Alternatively, the filter material can be a mixture or blend of polymer fibers, or a mixture or blend of polymer fibers and nonpolymeric fibers, for example, cellulose fibers obtained from wood pulp, purified cellulose, cotton fibers, or the like. A mixture of filter materials may be preferred in certain embodiments where it is desired to reduce materials costs, as polymeric materials may be more expensive than natural fibers. Any suitable proportion of polymeric material may be present, from 100% by weight polymeric material down to 80, 60, 50, 40, 30, 25, 20, 15, or 10% by weight or less polymeric material.

As discussed above, in certain embodiments it may be desirable to coat the filter material with one or more substances that may react chemically with an undesirable component of the smoke. Such substances may include natural or synthetic polymers, or chemicals known in the art to provide for a treated filter material capable of altering the chemistry of tobacco smoke. One method for coating the filter material is to prepare a solution or dispersion of the substance with a suitable solvent. Suitable solvents may include, for example, water, ethanol, acetone, methyl ethyl ketone, toluene, or the like.

The solution or dispersion can be applied to the surface of the filter material using gravure techniques, spraying techniques, printing techniques, immersion techniques, injection techniques, or the like. Most preferably, the filter material is essentially insoluble in the preferred solvent, and as such does not substantially affect the general structure of the filter material. After the solution or dispersion is applied to the surface of the filter material, the solvent is removed, typically by air-drying at room temperature or heating, for example, in a convection or forced-air oven. The amount of solution or dispersion which is

applied to the filter material is typically sufficient to cover the outer surface of the filter material, but not sufficient to fill the void spaces between the fibers of filter material.

Typically, the amount of solution or dispersion applied to the filter material is sufficient to deposit at least about 5 percent, preferably at least about 8 percent, more preferably at least about 10 percent, and most preferably at least about 15 percent of the substance, based on the weight of the filter material prior to treatment.

When the substance is a polymer, the polymer can be synthetic polymer or a natural polymer. Synthetic polymers are derived from the polymerization of monomeric materials (for example, addition or condensation polymers) or are isolated after chemically altering the substituent groups of a polymeric material. Natural polymers are isolated from organisms (for example, plants such as seaweed), usually by extraction.

Exemplary synthetic polymers that may be applied to filter materials include, but are not limited to, carboxymethylcellulose, hydroxypropylcellulose, cellulose esters such as cellulose acetate, cellulose butyrate and cellulose acetate propionate (for example, from Eastman Chemical Corp. of Kingsport, TN), polyethylene glycols, water dispersible amorphous polyesters with aromatic dicarboxylic acid functionalities (for example, Eastman AQs from Eastman Chemical Corp. of Kingsport, TN), ethylene vinyl alcohol copolymers (for example, from Mica Corp. of Shelton, CT), partially or fully hydrolyzed polyvinyl alcohols (for example, the Airvols from Air Products and Chemicals of Allentown, PA), ethylene acrylic acid copolymers (for example, Envelons from Rohm and Haas of Philadelphia, PA and Primacors from The Dow Chemical Co. of Wilmington, DE), polysaccharides (for example, Keltrol from CP Kelco of San Diego, CA), alginates (for example, from International Specialty Products of Wayne, NJ), carrageenans (for example, Viscarin GP109 and Nutricol GP120F konjac flour from FMC) and starches (for example, Nadex 772, K-4484 and N-Oil from National Starch & Chemical Co.).

Typically, natural or synthetic polymers tend to coat the surface of the filter material very efficiently, and have a high viscosity, making high coating levels unnecessary and sometimes difficult. Typically, certain natural or synthetic polymers can be applied to the filter material at levels of at least about 0.001 percent, preferably at least about 0.01 percent, more preferably at least about 0.1 percent, and most preferably at least about 1 percent, based on the weight of the filter material prior to treatment. Typically, the amount of certain natural or synthetic polymers applied to the filter material does not exceed about

10 percent, and normally does not exceed about 5 percent, based on the weight of the filter material prior to treatment.

The natural or synthetic polymeric material which is applied to the filter material can vary, depending upon factors such as the chemical functionality, hydrophilicity or hydrophobicity desired. If desired, more than one type of natural or synthetic polymer can be applied to the filter material in a single dispersion or solution. If desired, the filter material can have at least one type of natural or synthetic polymer dissolved or dispersed in a suitable solvent applied thereto and the solvent removed, after which the resulting coated filter material has at least one other natural or synthetic polymer applied in similar fashion. If multiple applications are conducted in this way, it is desirable that the solvent or solvents do not substantially dissolve any natural or synthetic polymer already coated onto the filter material.

Filters of preferred embodiments may include more than one segment. One configuration of such filters is the dual filter, wherein the filter constitutes two different segments, with one segment adjacent to the mouth and the other segment of the filter adjacent to the tobacco rod. A common type of dual filter is one wherein a cellulose acetate segment is situated on the mouth side of the filter, and a cellulose paper segment is situated on the side of the filter adjacent to the tobacco rod. Activated charcoal may be incorporated into the cellulose paper segment of the filter to assist in removal of undesired components from tobacco smoke.

Another filter configuration, referred to as a triple filter, has three segments, including a segment adjacent to the mouth, a segment adjacent to the tobacco rod, and a segment situated between the two other segments. The different segments may be prepared from different materials, or may be materials having the same composition but different physical form, for example, crimped sheet or tow, or may be materials having the same composition and physical form, but wherein one segment contains an additional component not present in another segment. A common triple filter configuration includes two segments selected from one or both of cellulose acetate and cellulose, one adjacent to the mouth and one adjacent to the filter, with a segment in between containing a smoke altering component. Examples of smoke altering components include activated carbon or other absorbents, or components imparting flavor to the smoke.

One variety of triple filter is the cavity filter. The cavity filter is composed of two segments separated by a cavity containing one or more smoke altering components. The cavity may contain an adsorbent material as described above, optionally in combination with other suitable components such as activated charcoal.

Dual and triple filters may be symmetrical (all filter segments are the same length) or asymmetrical (two or more segments are of different lengths). Filters may be recessed, with an open cavity on the mouth side, reinforced by an extra stiff plug wrap paper.

When the filter element contains a solid material in a form other than tow or sheet, it may be incorporated into the filter element using any suitable method or device, such as those described above for incorporating an absorbing, adsorbing, or reacting material into the filter element. Liquids may be incorporated into the porous filter material by immersing the filter material in the liquid, spraying the liquid onto the filter material, or combining the liquid with another component, for example, a component capable for forming a gel or a solid, then applying the liquid-containing substance to the porous filter material using methods well known to those skilled in the art.

The form of the filter material and the configuration of the filter material, as well as the filtration efficiency for particulate matter and vapor phase components of each segment of the filter element may be varied so as to yield the desired balance of performance characteristics for the filter element, as will be recognized by those skilled in the art. Filter materials in tow form can be processed and manufactured into filter rods using known techniques. Filter materials in sheet-like or web form can be formed into filter rods using techniques described in U.S. Pat. Nos. 4,807,809 to Pryor et al., and 5,074,320 to Jones, Jr. et al. Filter materials also can be formed into rods using a rod-making unit (for example, from Molins Tobacco Machinery, Ltd. of Bucks, United Kingdom).

The porous filter material may contain various additional minor components. These components may include pigments, dyes, preservatives, antioxidants, defoamers, solvents, lubricants, waxes, oils, resins, adhesives, and other materials, as are known in the art.

In a preferred embodiment, the smoking article is provided with a cavity filter composed of two cellulose acetate segments separated by a cavity containing activated charcoal, wherein the filter segments are wrapped in a paper plug wrap. The plug wrap may be provided with perforations in the cellulose acetate segment adjacent to the tobacco rod if air dilution is desired, for example, for low or ultra-low tar cigarettes. The cellulose acetate

segment adjacent to the tobacco rod is preferably about 9 mm in length, the mouth end segment is preferably 11 mm in length, and the cavity is preferably 5 mm in length. The cavity is preferably substantially filled. Substantially filled generally refers to a cavity segment wherein more than about 95 vol. % is filled with packed particles, preferably more than about 96, 97, 98, or 99 vol. % is filled with packed particles, and most preferably about 100 vol. % is filled with packed particles. However, in certain embodiments it may be desirable for the cavity to be less than substantially filled, for example, less than about 95, 94, 93, 92, 91, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 vol. % or less. In a preferred embodiment, the cavity is substantially filled with one type of activated charcoal. However, in certain other embodiments the activated charcoal may constitute a mixture of activated charcoals (for example, charcoals of varying particle size or source), or the activated charcoal may be mixed or combined with one or more inert ingredients, such as magnesium silicate (available as CAVIFLEX™ and SEL-X-4™ from Baumgartner, Inc. of Melbane, NC), inert carbon, or semolina. Most preferably, the cavity segment contains 0.1 g of a single type of activated charcoal as the sole component in a 5 mm long cavity segment of filter. In various embodiments various types of activated charcoal or carbon prepared from different starting materials, having different surface area and particle size, or having different properties may be preferred. Suitable activated carbons, including specialty activated carbons, may be obtained from Calgon Carbon Corporation of Pittsburgh, PA.

Additives

Additional components, as are known in the art, may also be added to the smokable material, or may be contained within the filter, the tobacco rod, or other components of the smoking articles of preferred embodiments. Nonlimiting examples of such components include tobacco extracts, lubricants, flavorings, and the like. These additional components preferably do not react with the microcapsules on the smoking material in such a way as to prematurely release their contents.

The filter element optionally can include a tobacco or flavor extract in intimate contact with the filter material. If desired, the tobacco or flavor extract can be spray dried and/or subjected to heat treatment. The filter element prior to smoking may include less than about 10% tobacco or flavor extract to more than 50% percent tobacco or flavor extract, based on the total dry weight of the filter element and extract. In some

embodiments, the tobacco Filter elements typically include a lubricating substance in intimate contact with the filter material. Normally, prior to smoking the cigarette, the filter element includes at least about 0.1 percent lubricating substance, based on the weight of the filter material of that segment. The lubricating substance can be a low molecular weight liquid (for example, glycerine) or a high molecular weight material (for example, an emulsifier).

Flavorants can be incorporated into the cigarette using conventional techniques familiar to the skilled artisan in addition to the microencapsulation technique described herein. If desired, flavor additives such as organic acids can be incorporated into the cigarette as additives to cut filler. See, for example, U.S. Pat. No. 4,830,028 to Lawson et al. If metallic or carbonaceous particles and nitrate or nitrite source are applied to the cut filler, it is preferred that they are added prior to addition of flavorants or flavor extract is between 15%, 20%, 25% or 30% and 35%, 40%, or 45%, of the total dry weight of the filter element and the extract.

The Smokable Material

The microcapsules may be applied to any suitable smokable material. Examples of preferred smokable materials are the tobaccos that include but are not limited to Oriental, Virginia, Maryland, and Burley tobaccos, as well as the rare and specialty tobaccos. The tobacco plant may be a variety produced through conventional plant breeding methods, or may be a genetically engineered variety. Low nicotine and/or low TSNA tobacco varieties, including genetically engineered varieties, are especially preferred. The tobacco may be cured using any acceptable method, including, but not limited to, flue-curing, air-curing, sun-curing, and the like, including curing methods resulting in low nitrosamine levels, such as the curing methods disclosed in U.S. Patent No. 6,202,649 and U.S. Patent No. 6,135,121 to Williams.

Generally, the tobacco material is aged. The cured or uncured tobacco may be subjected to any suitable processing step, including, but not limited to, microwave or other radiation treatment, treatment with ultraviolet light, or extraction with an aqueous or nonaqueous solvent.

The tobacco can be in the form of tobacco laminae, processed tobacco stems, reconstituted tobacco material, volume expanded tobacco filler, or blends thereof. The type of reconstituted tobacco material can vary. Certain suitable reconstituted tobacco materials

are described in U.S. Pat. No. 5,159,942 to Brinkley et al. Certain volume expanded tobacco materials are described in U.S. Pat. No. 5,095,922 to Johnson et al. Blends of the aforementioned materials and tobacco types can be employed. Exemplary blends are described in U.S. Pat. No. 5,074,320 to Jones, Jr. et al. Other smokable materials, such as those smokable materials described in U.S. Pat. No. 5,074,321 to Gentry et al., and 5,056,537 to Brown et al., also can be employed.

The smokable materials generally are employed in the form of cut filler as is common in conventional cigarette manufacture. For example, the smokable filler material can be employed in the form of pieces, shreds or strands cut into widths ranging from about 1/5 inch (5 mm) to about 1/60 inch (0.04 mm), preferably from about 1/20 inch (1.3 mm) to about 1/40 inch (0.6 mm). Generally, such pieces have lengths between about 0.25 inch (6 mm) and about 3 inches (76 mm). In certain embodiments, however, it may be preferred to use cut filler having widths more than about 1/5 inch (5 mm) or less than about 1/60 inch (0.04 mm), and lengths less than about 0.25 inch (6 mm) or more than about 3 inches (76 mm).

The smokable material can have a form (for example, a blend of smokable materials, such as a blend of various types of tobacco in cut filler form) having a relatively high nicotine content. Such a smokable material typically has a dry weight nicotine content above about 2.0%, 2.25%, 2.5%, 2.75%, or 3.0% or more. Such smokable materials are described in U.S. Pat. No. 5,065,775 to Fagg.

Alternatively, the smokable material can have a form having a relatively low or negligible nicotine content. Such a smokable material typically has a dry weight nicotine content below about 1.5%, 1.25%, 1.0%, 0.75%, 0.5%, 0.1%, 0.05% or less. Tobacco having a relatively low nicotine content is described in U.S. Pat. No. 5,025,812 to Fagg et al.

As used herein, the term "dry weight nicotine content" in referring to the smokable material is meant the mass alkaloid nicotine as analyzed and quantitated by spectroscopic techniques divided by the dry weight of the smokable material analyzed. See, for example, Harvey et al., *Tob. Sci.*, Vol. 25, p. 131 (1981).

In a preferred embodiment, the smokable material constitutes a tobacco product obtained from tobacco plants that are substantially free of nicotine and/or tobacco-specific nitrosamines (TSNAs). Tobaccos that may be substantially free of nicotine or TSNAs may

be produced by interrupting the ability of the plant to synthesize nicotine using genetic engineering. Copending provisional application Ser. No. 60/297,154 filed 06/08/01, filed June 8, 2001 and WO9856923 to Conkling et al. (both incorporated herein by reference in their entirety) describe tobacco that is substantially free of nicotine and TSNAs that is made by exposing at least one tobacco cell of a selected variety to an exogenous DNA construct having, in the 5' to 3' direction, a promoter operable in a plant cell and DNA containing a portion of a DNA sequence that encodes an enzyme in the nicotine synthesis pathway. The DNA is operably associated with the promoter, and the tobacco cell is transformed with the DNA construct, the transformed cells are selected, and at least one transgenic tobacco plant is regenerated from the transformed cells. The transgenic tobacco plants contain a reduced amount of nicotine and/or TSNAs as compared to a control tobacco plant of the same variety. In preferred embodiments, DNA constructs having a portion of a DNA sequence that encodes an enzyme in the nicotine synthesis pathway may have the entire coding sequence of the enzyme, or any portion thereof.

In a preferred embodiment, the smokable material constitutes a tobacco product obtained from tobacco plants that have reduced nicotine content and/or TSNAs such as those described in copending provisional application Ser. No. 60/229,198, filed August 30, 2000 (incorporated herein by reference in its entirety).

Tobacco products having specific amounts of nicotine and/or TSNAs may be created through blending of low nicotine/TSNA tobaccos such as those described above with conventional tobaccos. Some blending approaches begin with tobacco prepared from varieties that have extremely low amounts of nicotine and/or TSNAs. By blending prepared tobacco from a low nicotine/TSNA variety (for example, undetectable levels of nicotine and/or TSNAs) with a conventional tobacco (for example, Burley, which has 30,000 parts per million (ppm) nicotine and 8,000 parts per billion (ppb) TSNA; Flue-Cured, which has 20,000 ppm nicotine and 300 ppb TSNA; and Oriental, which has 10,000 ppm nicotine and 100 ppb TSNA), tobacco products having virtually any desired amount of nicotine and/or TSNAs can be manufactured. Tobacco products having various amounts of nicotine and/or TSNAs can be incorporated into tobacco use cessation kits and programs to help tobacco users reduce or eliminate their dependence on nicotine and reduce the carcinogenic potential.

For example, a step 1 tobacco product can constitute approximately 25% low nicotine/TSNA tobacco and 75% conventional tobacco; a step 2 tobacco product can constitute approximately 50% low nicotine/TSNA tobacco and 50% conventional tobacco; a step 3 tobacco product can constitute approximately 75% low nicotine/TSNA tobacco and 25% conventional tobacco; and a step 4 tobacco product can constitute approximately 100% low nicotine/TSNA tobacco and 0% conventional tobacco. A tobacco use cessation kit can include an amount of tobacco product from each of the aforementioned blends to satisfy a consumer for a single month program. That is, if the consumer is a one pack a day smoker, for example, a single month kit provides 7 packs from each step, a total of 28 packs of cigarettes. Each tobacco use cessation kit may include a set of instructions that specifically guide the consumer through the step-by-step process. Of course, tobacco products having specific amounts of nicotine and/or TSNA may be made available in conveniently sized amounts (for example, boxes of cigars, packs of cigarettes, tins of snuff, and pouches or twists of chew) so that consumers could select the amount of nicotine and/or TSNA they individually desire. There are many ways to obtain various low nicotine/low TSNA tobacco blends using the teachings described herein and the following is intended merely to guide one of skill in the art to one possible approach.

To obtain a step 1 tobacco product, which is a 25% low nicotine/TSNA blend, prepared tobacco from an approximately 0 ppm nicotine/TSNA tobacco can be mixed with conventional Burley, flue-cured, or Oriental in a 25%/75% ratio respectively to obtain a Burley tobacco product having 22,500 ppm nicotine and 6,000 ppb TSNA, a flue-cured product having 15,000 ppm nicotine and 225 ppb TSNA, and an Oriental product having 7,500 ppm nicotine and 75 ppb TSNA. Similarly, to obtain a step 2 product, which is 50% low nicotine/TSNA blend, prepared tobacco from an approximately 0 ppm nicotine/TSNA tobacco can be mixed with conventional Burley, flue-cured, or Oriental in a 50%/50% ratio respectively to obtain a Burley tobacco product having 15,000 ppm nicotine and 4,000 ppb TSNA, a flue-cured product having 10,000 ppm nicotine and 150 ppb TSNA, and an Oriental product having 5000 ppm nicotine and 50 ppb TSNA. Further, a step 3 product, which is a 75%/25% low nicotine/TSNA blend, prepared tobacco from an approximately 0 ppm nicotine/TSNA tobacco can be mixed with conventional Burley, flue-cured, or Oriental in a 75%/25% ratio respectively to obtain a Burley tobacco product having 7,500

ppm nicotine and 2,000 ppb TSNA, a flue-cured product having 5,000 ppm nicotine and 75 ppb TSNA, and an Oriental product having 2,500 ppm nicotine and 25 ppb TSNA.

It is appreciated that tobacco products are often a blend of many different types of tobaccos, which were grown in many different parts of the world under various growing conditions. As a result, the amount of nicotine and TSNAs may differ from crop to crop. Nevertheless, by using conventional techniques one can easily determine an average amount of nicotine and TSNA per crop used to create a desired blend. By adjusting the amount of each type of tobacco that makes up the blend one of skill can balance the amount of nicotine and/or TSNA with other considerations such as appearance, flavor, and smokability. In this manner, a variety of types of tobacco products having varying level of nicotine and/or nitrosamine, as well as, appearance, flavor and smokability can be created.

While in the preferred embodiments the microcapsules are applied to a smokable material including tobacco, any other smokable materials may preferred in other embodiments. For example, the microcapsules may be applied to smokable plant materials as are commonly preferred in various herbal smoking materials. Mullein and Mugwort are commonly preferred base materials in blends of herbal smoking materials. Some other commonly preferred plant materials that are also smokable materials include Willow bark, Dogwood bark, Pipsissewa, Pyrola, Kinnikinnik, Manzanita, Madrone Leaf, Blackberry, Raspberry, Loganberry, Thimbleberry, and Salmonberry.

The microencapsulated flavorant of preferred embodiments may be applied to any smokable material in order to provide improved taste to the smokable material. However, the preferred flavorant or flavorants, as well as the amount of such flavorants may vary depending upon the type of smokable material used.

The Wrapping Material

The wrapping material which circumscribes the charge of smokable material can vary. Examples of suitable wrapping materials are cigarette paper wrappers available from Schweitzer-Mauduit International in Alpharetta, Georgia. Cigarette paper wraps the column of tobacco in a cigarette and can be made from flax, wood, or a combination of fibers. Certain properties such as basis weight, porosity, opacity, tensile strength, texture, ash appearance, taste, brightness, good gluing, and lack of dust are selected to provide optimal performance in the finished product, as well as to meet runnability standards of the high-speed production processes preferred by cigarette manufacturers.

A more porous paper is one that allows air to easily pass into a cigarette. Porosity is measured in Coresta units and can be controlled to determine the rate and direction of airflow through the cigarette. The higher the number of Coresta units, the more porous the paper. Tar and nicotine yields are commonly controlled without altering the flavor of the cigarette through the choice of paper. The use of highly porous papers can help create lower tar levels in the cigarette. Higher paper porosity increases the combustibility of a cigarette by adding more air to the process, which increases the heat and the burning rate. A higher burn rate may lower the number of puffs that a smoker takes per cigarette. Papers having porosities up to 200 Coresta units or higher are generally preferred, however different kinds of cigarettes may use papers of preferred porosities. For example, American-blend cigarettes typically use 40 to 50 Coresta unit papers. Flue-cured tobacco cigarettes, which burn slower, generally use higher porosities, ranging from 60 to 80 Coresta unit papers. Higher porosities may be obtained by electronically perforating (EP) the paper.

Cigarette papers are available that are prepared from various base fibers. Flax and wood are commonly preferred base fibers. In addition to 100% flax and 100% wood papers, papers are also available with flax and wood fibers mixed in various ratios. Wood based papers are widely preferred because of their low cost, however certain consumers prefer the taste of flax based papers.

Suitable cigarette papers may be obtained from RFS (US) Inc., a subsidiary of privately-held PURICO (IOM) Limited of the United Kingdom, which is the current owner of P. H. Glatfelter Company's Ecusta mill which manufactures tobacco papers. In preferred embodiments, a paper having a porosity of about 26 Coresta EP to 90 Coresta EP is preferred. Suitable papers include Number 409 papers having a porosity of 26 Coresta and 0.85% citrate content, and Number 00917 papers having a porosity of 26 Coresta EP. However, in certain embodiments, it may be preferred to use a paper having a lower air permeability, for example, a paper that has not been subjected to electronic perforation and which has a low inherent porosity, for example, less than 26 Coresta.

In preferred embodiments, the cigarette paper is suitable for use in "self-extinguishing" cigarettes. Examples of cigarette papers suitable for use in self-extinguishing cigarettes include, for example, papers saturated with a citrate or phosphate

fire retardant or incorporating one or more fire retardant bands along the length of the paper. Such papers may also be thicker papers of reduced flammability.

Wrapping materials described in U.S. Pat. No. 5,220,930 to Gentry may be preferred in certain embodiments. More than one layer of circumscribing wrapping material can be employed, if desired. See, for example, U.S. Pat. No. 5,261,425 to Raker et al. Other wrapping material includes plug wrap paper and tipping paper. Plug wrap paper wraps the outer layer of the cigarette filter plug and holds the filter material in cylindrical form. Highly porous plug wrap papers are preferred in the production of filter-ventilated cigarettes.

Tipping paper joins the filter element with the tobacco rod. Tipping papers are typically made in white or a buff color, or in a cork pattern, and are both printable and glueable at high speeds. Such tipping papers are used to produce cigarettes that are distinctive in appearance, as well as to camouflage the use of activated carbon in the filter element. Pre-perforated tipping papers are commonly preferred in filter-ventilated cigarettes.

In the case of cigars, reconstituted tobacco wrapper is often wrapped around the outside of machine-made cigars to provide a uniform, finished appearance. The wrapper material can incorporate printed veins to give the look of natural tobacco leaf. Such wrapper material is manufactured utilizing tobacco leaf by-products. Reconstituted tobacco binder holds the "bunch" or leaves of tobacco in a cylindrical shape during the production of machine-made cigars. It is also manufactured utilizing tobacco leaf by-products.

An extremely small amount of a sideseam adhesive is preferred to secure the ends of the cigarette paper wrapper around the tobacco rod (and filter element, if present). Any suitable adhesive may be used. In a preferred embodiment, the sideseam adhesive is an emulsion of ethylene vinyl acetate copolymer in water.

The cigarette wrapper may include extremely small amounts of inks containing oils, varnishes, pigments, dyes, and processing aids, such as solvents and antioxidants. Ink components may include such materials as linseed varnish, linseed oil polymers, white mineral oils, clays, silicas, natural and synthetic pigments, and the like, as are known in the art.

Smoking Articles

The smoking articles of the preferred embodiments may have various forms. Preferred smoking articles may be typically rod-shaped, including, for example, cigarettes and cigars. In addition, the smoking article may be tobacco for a pipe. For example, the smoking article can have the form of a cigarette having a smokable material (for example, tobacco cut filler) wrapped in a circumscribing paper wrapping material. Exemplary cigarettes are described in U.S. Pat. Nos. 4,561,454 to Guess. In a preferred embodiment, the smoking article is a cigarette having a smokable filter material or tobacco rod.

In another preferred embodiment, a cigarette is provided which yields relatively low levels of "tar" per puff on average when smoked under FTC smoking conditions (for example, an "ultra low tar" cigarette).

In another preferred embodiment, a cigarette is provided having a smokable filler material or tobacco rod having a relatively low or negligible nicotine content, and a filter element.

In another preferred embodiment, a cigarette is provided having a smokable filler material or tobacco rod having a relatively low TSNA content, and a filter element.

The amount of smokable material within the tobacco rod can vary, and can be selected as desired. Packing densities for tobacco rods of cigarettes are typically between about 150 and about 300 mg/cm³, and are preferably between about 200 and about 280 mg/cm³, however, higher or lower amounts may be preferred for certain embodiments.

Typically, a tipping material circumscribes the filter element and an adjacent region of the smokable rod such that the tipping material extends about 3 mm to about 6 mm along the length of the smokable rod. Typically, the tipping material is a conventional paper tipping material. The tipping material can have a porosity which can vary. For example, the tipping material can be essentially air impermeable, air permeable, or can be treated (for example, by mechanical or other perforation techniques) so as to have a region of perforations, openings or vents, thereby providing a means for providing air dilution to the cigarette. The total surface area of the perforations and the positioning of the perforations along the periphery of the cigarette can be varied in order to control the performance characteristics of the cigarette.

The mainstream cigarette smoke may be diluted with air from the atmosphere via the natural porosity of the cigarette wrapper and/or tipping material, or via perforations,

openings, or vents in the cigarette wrapper and/or tipping material. Air dilution means may be positioned along the length of the cigarette, typically at a point along the filter element which is at a maximum distance from the extreme mouth-end thereof. The maximum distance is dictated by factors such as manufacturing constraints associated with the type of tipping employed and the cigarette manufacturing apparatus and process. For example, for a filter element having a 27 mm length, the maximum distance may be between about 23 mm and about 26 mm from the extreme mouth-end of the filter element. In a preferred aspect, the air dilution means is positioned toward the extreme mouth-end of the cigarette relative to the smoke-altering filter segment. For example, for a filter element having a 27 mm length including a smoke-altering filter segment of 12 mm length and a mouth-end segment of 15 mm, a ring of air dilution perforations can be positioned either 13 mm or 15 mm from the extreme mouth-end of the filter element.

As used herein, the term "air dilution" is the ratio (generally expressed as a percentage) of the volume of air drawn through the air dilution means to the total volume of air and smoke drawn through the cigarette and exiting the extreme mouth-end portion of the cigarette. For air diluted or ventilated cigarettes, the amount of air dilution can vary. Generally, the amount of air dilution for an air-diluted cigarette is greater than about 10 percent, typically greater than about 20 percent, and often greater than about 30 percent. Typically, for cigarettes of relatively small circumference (namely, about 21 mm or less) the air dilution can be somewhat less than that of cigarettes of larger circumference. The upper limit of air dilution for a cigarette typically is less than about 85 percent, more frequently less than about 75 percent. Certain relatively high air diluted cigarettes have air dilution amounts of about 50 to about 75 percent, often about 55 to about 70 percent.

Cigarettes of certain embodiments may yield less than about 0.9, often less than about 0.5, and usually between about 0.05 and about 0.3 FTC "tar" per puff on average when smoked under FTC smoking conditions (FTC smoking conditions include 35 ml puffs of 2 second duration separated by 58 seconds of smolder). Such cigarettes are "ultra low tar" cigarettes which yield less than about 7 mg FTC "tar" per cigarette. Typically, such cigarettes yield less than about 9 puffs, and often about 6 to about 8 puffs, when smoked under FTC smoking conditions. While "ultra low tar" cigarettes are generally preferred, in certain embodiments, however, cigarettes providing less than about 0.05 or more than about 0.9 FTC "tar" per puff are contemplated.

In certain embodiments, cigarettes yielding a low or negligible amount of nicotine are provided. Such cigarettes generally yield less than about 0.1, often less than about 0.05, frequently less than about 0.01, and even less than about 0.005 FTC nicotine per puff on average when smoked under FTC smoking conditions. In other embodiments, a cigarette delivering higher levels of nicotine may be desired. Such cigarettes may deliver about 0.1, 0.2, 0.3, or more FTC nicotine per puff on average when smoked under FTC smoking conditions.

Cigarettes yielding a low or negligible amount of nicotine may yield between about 1 mg and about 20 mg, often about 2 mg to about 15 mg FTC "tar" per cigarette; and may have relatively high FTC "tar" to FTC nicotine ratios of between about 20 and about 150.

Cigarettes of the preferred embodiments may exhibit a desirably high resistance to draw, for example, a pressure drop of between about 50 and about 200 mm water pressure at 17.5 cc/sec of air flow. Typically, pressure drop values of cigarettes are measured using instrumentation available from Cerulean (formerly Filtrona Instruments and Automation) of Milton Keynes, United Kingdom. Cigarettes of preferred embodiments preferably exhibit resistance to draw values of about 70 to about 180, more preferably about 80 to about 150 mm water pressure drop at 17.5 cc/sec of airflow.

Cigarettes of preferred embodiments may include a smoke-altering filter segment. The smoke-altering filter segment may reduce one or more undesirable components in the smoke, and/or may provide an enhanced tobacco smoke flavor, a richer smoking character, enhanced-mouthfeel and increased smoking satisfaction, as well as improvement of the perceived draw characteristics of the cigarette.

The above description provides several methods and materials of the present invention. This invention is susceptible to modifications in the methods and materials, such as the choice of flavorant, encapsulant, and the like, as well as alterations in the fabrication methods and equipment. Such modifications will become apparent to those skilled in the art from a consideration of this disclosure or practice of the invention disclosed herein. Consequently, it is not intended that this invention be limited to the specific embodiments disclosed herein, but that it cover all modifications and alternatives coming within the true scope and spirit of the invention as embodied in the attached claims.

Every patent and other reference mentioned herein is hereby incorporated by reference in its entirety.

WHAT IS CLAIMED IS:

1. A smoking composition comprising a smokable material, a plurality of microcapsules, and a filter, the smoking composition comprising a cigarette, wherein the smokable material comprises a tobacco, the filter comprises an activated charcoal or an activated carbon, and the microcapsules comprise a shell material and a filler material, wherein the filler material comprises menthol, and wherein the shell material comprises a waxy thermomelttable material having a melting point of from about 35°C to about 200°C.

2. A smoking composition comprising a smokable material and a plurality of microcapsules, the microcapsules comprising a shell material and a filler material, wherein the shell material melts upon exposure to a temperature above an ambient temperature and below a pyrolysis temperature of the smokable material, whereby the filler material is released into a mainstream smoke, a sidestream smoke, or both the mainstream smoke and the sidestream smoke.

3. The composition of claim 2, wherein the smokable material comprises tobacco.

4. The composition of claim 2, wherein the tobacco has a reduced or a negligible nicotine content.

5. The composition of claim 2, wherein the tobacco has a reduced or a negligible content of a tobacco-specific nitrosamine.

6. The composition of claim 2, wherein the filler material comprises a flavorant.

7. The composition of claim 6, wherein the flavorant comprises menthol.

8. The composition of claim 2, wherein the smoking composition further comprises a filter.

9. The composition of claim 8, wherein the filter further comprises an activated charcoal or an activated carbon.

10. The composition of claim 9, wherein the filter comprises a cavity filter.

11. The composition of claim 9, wherein the cavity filter is at least 95 vol. % filled.

12. The composition of claim 9, wherein the cavity filter is about 100 vol. % filled.

13. The composition of claim 2, wherein the shell material comprises a waxy thermomelttable material having a melting point of from about 35°C to about 200°C.

14. The composition of claim 13, wherein the waxy thermomelttable material is selected from the group consisting of carnauba wax, montan wax, ouricury wax, candelilla wax, coconut wax, paraffin wax, beeswax, spermaceti wax, microcrystalline wax, rice wax, low molecular weight polyethylene wax, stearic acid, palmitic acid, myristic acid, stearylamine, stearone, and mixtures thereof.

15. The composition of claim 2, wherein the shell material comprises a water insoluble polymer.

16. The composition of claim 15, wherein the water insoluble polymer is selected from the group consisting of cellulose ethers, cellulose esters, ureaformaldehyde resins, polyvinyl chloride, polyvinylidene chloride, polyethylene, polypropylene, polyacrylates, polymethacrylates, polymethyl-methacrylates, nylon, and mixtures thereof.

17. The composition of claim 2, wherein the shell material comprises a water soluble polymer.

18. The composition of claim 17, wherein the water soluble polymer is selected from the group consisting of polyvinyl pyrrolidone, water soluble celluloses, polyvinyl alcohol, ethylene maleic anhydride copolymer, methyl vinyl ether maleic anhydride copolymer, polyethylene oxides, water soluble polyamide, water soluble polyesters, polymers of acrylic acid, polystyrene acrylic acid copolymers, and mixtures thereof.

19. The composition of claim 2, wherein the shell material is selected from the group consisting of starch, gums, gelatin, dextrans, hydrolyzed gums, hydrolyzed gelatin, gum arabic, larch, pectin, tragacanth, locust bean, guar, alginates, carrageenans, carboxy methyl cellulose, karaya, maltodextrins, and mixtures thereof.

20. A method for providing a smokable material comprising a volatile flavorant, the method comprising:

providing a plurality of microcapsules comprising a shell material and a filler material, the filler material comprising a volatile flavorant, wherein the shell material melts upon exposure to a temperature above an ambient temperature and below a pyrolysis temperature of the smokable material; and

depositing the microcapsules on the smokable material, whereby a smokable material comprising a volatile flavorant is obtained.

21. The method of claim 21, wherein the smokable material comprises tobacco.
22. The method of claim 21, wherein the volatile flavorant comprises menthol.
23. The method of claim 21, wherein the shell material comprises a waxy thermomeltable material having a melting point of from about 35°C to about 200°C.

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(54) Title: METHOD AND COMPOSITION FOR MENTHOLATION OF CHARCOAL FILTERED CIGARETTES

(57) Abstract: The present invention relates to smoking articles such as cigarettes, and in particular to a method and composition for mentholation of smoking articles, including microencapsulation of menthol or other flavorants in a material melting below the pyrolysis zone of the smoking article.



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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 1 574 645 A (THE NATIONAL CASH REGISTER COMPANY) 11 July 1969 (1969-07-11)	1
X	claims; examples	2,3,6,7, 17,19-22
A	GB 1 349 537 A (IMP GROUP LTD) 3 April 1974 (1974-04-03)	1
X	figure 3; example 1	2,3,6-8, 17,19-22
Y		9-12
Y	US 3 658 069 A (WISE HENRY ET AL) 25 April 1972 (1972-04-25) the whole document	9-12
A	US 5 000 198 A (NAKAJIMA MITUO) 19 March 1991 (1991-03-19) claims	1
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/35741

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 628 260 A (REYNOLDS TOBACCO CO R) 14 December 1994 (1994-12-14) page 5, line 39 - line 50; claims ---	1
A	WO 00 33676 A (YOON DONG SEOK) 15 June 2000 (2000-06-15) claims ---	4
A	US 6 135 121 A (WILLIAMS JONNIE R) 24 October 2000 (2000-10-24) claims ---	5
A	EP 0 464 324 A (JAPAN TOBACCO INC) 8 January 1992 (1992-01-08) -----	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 02/35741

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claim : 1

Smoking composition comprising a smokable material, a plurality of microcapsules containing menthol and a filter comprising activated charcoal or active carbon, the shell material of the microcapsules being a waxy thermomelttable material having a melting point of from 35 C to 200 C.

2. Claims: 2-23

A smoking composition comprising a smokable material and a plurality of microcapsules comprising a shell material and a filler material, wherein the shell material melts upon exposure to a temperature above the ambient temperature and below a pyrolysis temperature of the smokable material whereby the filler is released in mainstream and/or sidestream smoke.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/35741

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